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Environmental Assessment of Solid Residues from Fluidized-Bed Fuel Processing

Ralph Stone and Co, Inc, Los Angeles, Calif.

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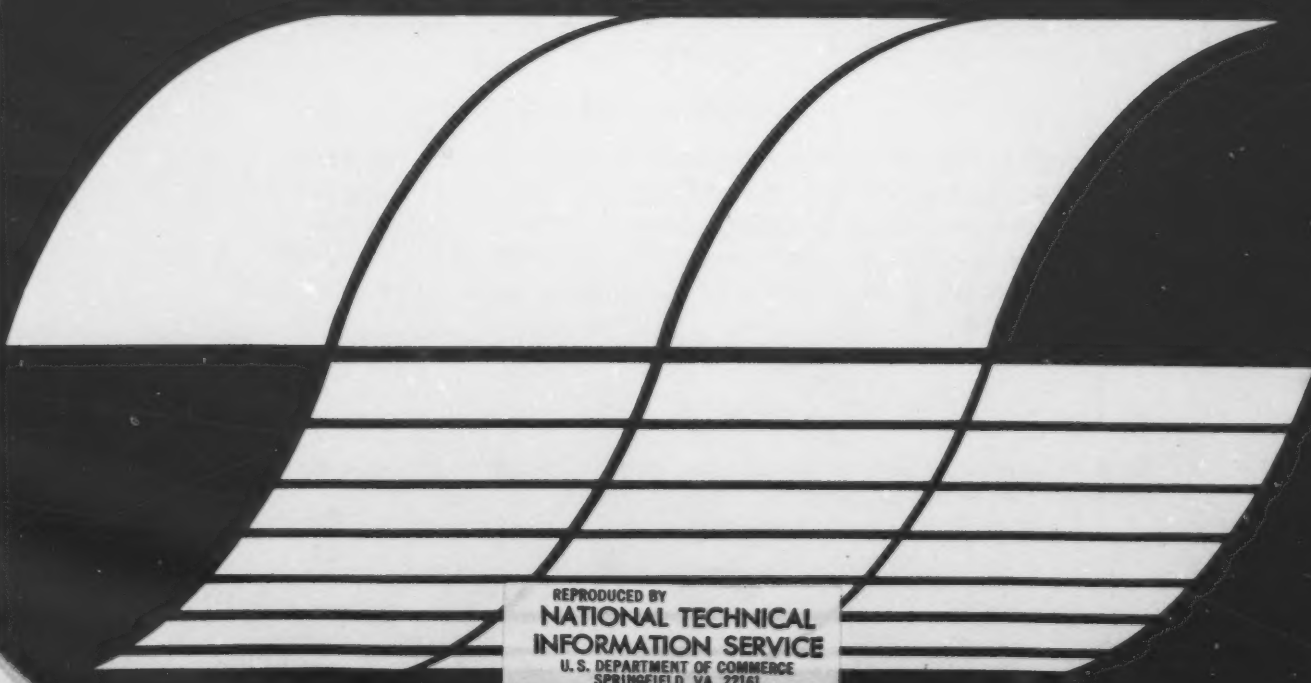
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ENVIRONMENTAL ASSESSMENT OF SOLID RESIDUES FROM FLUIDIZED-BED FUEL PROCESSING

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Program Report



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ENVIRONMENTAL ASSESSMENT OF SOLID RESIDUES FROM FLUIDIZED-BED FUEL PROCESSING

by

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**Contract No. 68-03-2347
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**Industrial Environmental Research Laboratory
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Research Triangle Park, N.C. 27711**

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ABSTRACT

This report presents results for the first 15 months of an environmental assessment of the solid residues generated by fluidized-bed coal combustion and oil gasification. Tasks included a literature search, chemical and physical residue characterization, laboratory leaching studies, and testing of residues in various materials and agricultural applications.

The literature search reviewed current fluidized-bed combustion technology, identified products in which residues might be used, and provided data on typical soil and geologic conditions at the disposal sites being evaluated. Laboratory tests included total chemical characterization, composition of acid-, base-, and water-soluble fractions, cation exchanged capacity, BOD, temperature change from water addition, particle size distribution, dry density, specific gravity, permeability, water-holding capacity, moisture content, and small-scale column leaching studies.

Pilot-scale columns simulated abandoned coal mines, dolomite and limestone quarries, sanitary landfills, soils, and the ocean. Water was added to columns on a prescribed schedule and the resulting leachate was collected and analyzed for chemical constituents. The data were used to assess the potential for impact on water quality, and the capacity of the disposal environment to attenuate degradation.

Product tests and preliminary market analyses were conducted for residue use in concrete, asphalt, soil cement, and lime/fly ash aggregate. Uses as acid mine drainage neutralizer and agricultural soil conditioner/ fertilizer were also evaluated.

This annual report was submitted in partial fulfillment of Contract No. 68-03-2347 by Ralph Stone and Company, Inc., under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period from November 5, 1975 to December 31, 1976. Further work continues to be performed and will be summarized in future reports.

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CHAPTER 1 INTRODUCTION

Background

Total electricity consumption in the United States is projected to increase at an annual rate of 7 to 8 percent over 1970-1990. The relative shares of coal, oil, gas, and hydroelectric generation are expected to decrease as nuclear sources come to predominate. These trends are shown in Tables 1 and 2. However, the absolute quantities of coal and oil used should increase along with total consumption. Projected fuel usage requirements are shown in Table 3.

Combustion of more coal and oil implies increased sulfur oxides generation, as shown in Table 4. This may be aggravated by a projected increase in the average sulfur content of coal burned, from the current 2.7 percent to 3.5 percent by the year 2000. Airborne sulfur compounds are associated with damage to human health, vegetation, and materials. There are many ways being researched to reduce sulfur oxide emissions, as shown in Table 5.

One approach to alleviating the problem is to develop ways of burning high sulfur fuels without high-sulfur oxide emissions. Among the options being researched are fluidized-bed combustion of high sulfur coal and fluidized-bed gasification of high sulfur residual oils. The EPA is evaluating two high sulfur coal fluidized-bed combustion pilot plants. The U.S. Energy Research and Development Administration (ERDA) is supporting one small scale and one large scale pilot plant. One high sulfur residual oil fluidized-bed reactor pilot plant is being operated in England under an EPA international agreement. In these plants, either pulverized limestone or dolomite bed material is admixed to the coal or oil being burned. The sulfur in the fuels reacts with the bed material to form calcium and magnesium sulfates and, to some degree, sulfites and sulfides. Gaseous sulfur emissions are thus greatly reduced, but solid residues are increased. These residues consist of calcium and magnesium oxides (from unreacted portions of dolomite and limestone), calcium and magnesium sulfur compounds, traces of unburned coal and oil and their stack and bottom ash, and inert matter originated from natural dolomite or limestone.

The disposal of these residues is a matter of concern. For example, toxic substances might be leached from the residues into ground or surface waters. This study was initiated because there had been no extensive research into the environmental impacts of the disposal of these solid residues or the feasibility of their recovery.

TABLE 1. U. S. ELECTRIC GENERATING CAPACITY

Type of Plant	1970(Actual)		1980 (Projected)		1990 (Projected)	
	Capacity (10 ³ Mw)	% of Total	Capacity (10 ³ Mw)	% of Total	Capacity (10 ³ Mw)	% of Total
Fossil steam	260	76	393	59	557	44
Nuclear steam	6	2	147	22	500	40
Steam subtotal	266	78	540	81	1,057	84
Hydroelectric - conventional	52	15	68	10	82	6
Hydroelectric - pumped storage	4	1	27	4	71	6
Gas turbine and diesel	19	6	31	5	51	4
Totals	341	100	666	100	1,261	100

Source: 159 .

TABLE 2. U. S. ELECTRICITY GENERATION BY TYPE OF FUEL - 1970-1990

Year	Percent of Total Generation				
	Coal	Oil	Gas	Nuclear	Hydroelectric
1970	46.4	11.8	24.2	1.4	16.2
1980	36.5	12.4	12.4	27.6	11.1
1990	26.7	8.0	7.2	47.3	10.8

Source: 159 .

TABLE 3. PROJECTED ANNUAL FUEL REQUIREMENTS:
STEAM ELECTRIC POWER PLANTS

Fuel	Unit	1970	1980	1990
Coal	10^6 kkg	292	454	635
Natural gas	10^9 cu m	185	106	118
Residual fuel oil	10^6 bbl	331	640	800
Uranium ore	kkg ^a	6,800	37,000	115,000

^a kkg of U_3O_8 required to supply feed for diffusion plants without plutonium recycle.

Source: 158.

TABLE 4. POTENTIAL U. S. SULFUR DIOXIDE POLLUTION
WITH NO ABATEMENT

Source	Annual Emission of SO_2 (kkg)				
	1967	1970	1980	1990	2000
Power plant operation (coal and oil)	13.6	18.1	37.3	56.2	85.7
Other combustion of coal	4.6	4.4	3.6	2.8	1.5
Combustion of petroleum products (excluding power plant oil)	2.5	3.1	3.5	3.9	4.6
Smelting of metallic ores	3.4	3.6	4.8	6.4	8.7
Petroleum refinery operation	1.9	2.2	3.6	5.9	9.5
Miscellaneous sources ^a	1.8	1.8	2.4	3.1	4.1
Total	27.9	22.2	55.2	78.4	114.1

^a Includes coke processing, H_2SO_4 plants, coal refuse banks, refuse incineration, and pulp and paper manufacturing.

Source: 160.

TABLE 5. SULFUR DIOXIDE ABATEMENT PROCESSES

1. Precombustion processes
 - a. Coal and oil cleaning
 - b. Coal and oil gasification
 - c. Fluidized bed gasification
2. Combustion processes
 - a. Fluidized bed combustion
 - b. Black, Sivalis, and Bryson
3. Limestone processes
 - a. Wet scrubbing
 - b. Dry removal
4. Processes for sulfur recovery from stack gases
 - a. Cat - O_x
 - b. Wellman-Lord
 - c. Esso-Babcock & Wilcox adsorbent
 - d. Formate scrubbing
 - e. Ammonia scrubbing
 - f. Westvaco char
 - g. Molten carbonate
 - h. Sodium bicarbonate adsorption
 - i. Modified Claus
 - k. Catalytic chamber
 - l. Ionics/Stone & Webster
 - m. Alkalized alumina

Objectives

The general objective of this project was to assess the environmental impact of the disposal or the recovery of the residues which would be generated with widespread commercial use of the fluidized-bed process for high sulfur coal combustion and gasification of high sulfur residual oil. Specific objectives were to:

- Determine the chemical and physical characteristics of the residues from the fluidized bed process applied to coal and oil.
- Identify the leachate water pollution constituents and quantities resulting from land disposal of residues.
- Evaluate the potential effects of disposing the residues into different soil and sedimentary environments and into the ocean.
- Investigate the potential for recovery of the solid residues.
- Determine the needs for treating the residues and establishing methods for the disposal of such wastes.

Scope of Work

Literature reviews, laboratory studies, and pilot test columns were used during Year 01 to determine the potential environmental impacts from disposal of solid residues from fluidized-bed operations. Residues from both the fluidized-bed combustion of high sulfur coal and fluidized bed gasification of high sulfur residual oils were tested. Residues are being obtained from three pilot plants. The residues received are identified in Table 6; the symbol abbreviations shown will be used throughout the report in reference to the three pilot plants.

In general, the literature search provided information on the disposal and environmental impacts of similar residues such as coal ash or limestone SO_x scrubber wastes. Information on similar types of waste residues were obtained in laboratory and pilot test reports. From available sources, estimates were made of the conditions for and the levels of pollutants anticipated from the residue wastes in various environments. Process descriptions of material flows for plants generating residues were obtained. Typical natural conditions were selected for our study work. The results of the literature search were of value in designing the specific limits and goals on the laboratory and column tests.

The laboratory studies were used to duplicate a range of theoretical disposal environments on a small scale. Residues were tested under controlled conditions; environmental variables were controlled to duplicate many real conditions that could affect the behavior of the residues in natural environments. All leachate was collected and analyzed.

TABLE 6. IDENTIFICATION OF RESIDUES

Symbol	Residue Source	Descriptive Name of Residue	Pilot Plant Location
CFA	Oil	Cyclone fly ash	Esso; Abingdon, England
FSFA	Oil	Fines, stack, regenerator, gasifier, fly ash	Esso; Abingdon, England
VFA	Coal	Virginia fly ash	Pope, Evans, and Robbins; Alexandria, Virginia
VSBM	Coal	Virginia spent bed material	Pope, Evans, and Robbins; Alexandria, Virginia
NJFA	Coal	New Jersey fly ash	Exxon; Linden, New Jersey
NJSBM	Coal	New Jersey spent bed material	Exxon; Linden, New Jersey
EFA	Oil	English fly ash	Esso; Abingdon, England
ESBM	Oil	English spent bed material	Esso; Abingdon, England

Profiles of the residues for different disposal methods have been determined. The results of the laboratory studies were used to design the test columns. Table 44 presents information on the residues used in the laboratory and test column studies.

The field work will attempt to verify the results of the laboratory and column studies in natural environments. To do so, test plots will be constructed in the natural environments, and leachate monitoring probes and wells will be installed. Records will be kept of environmental conditions, and leachate and groundwater quality will be monitored. Analyses will be conducted to determine those disposal site factors which can minimize adverse environmental impacts.

Studies were also undertaken to determine the possibility of recovering and marketing the residues instead of disposing of them. Laboratory tests are being conducted to determine the feasibility of using these residues for commercial products. These tests compare the properties of materials produced using residues with those made with conventional raw materials. A preliminary market study was initiated to determine the market potentials for the residues and their finished products.

Concurrent with the product feasibility task, an evaluation of requirements for treating residues was initiated to establish whether treatment can enhance product use or is required for disposal. The disposal needs for liquid wastes was also investigated in terms of environmental impacts.

The Rivesville, West Virginia field test area was selected by first identifying potential sites from literature, from our company knowledge, and from the EPA. Mail and telephone contacts were used to help screen candidate sites for local conditions and cooperation. A preliminary two-day visit was made to the Rivesville area. The preliminary visit reviewed available facilities and transportation requirements.

CHAPTER 2

SUMMARY

Introduction

The overall purpose of the proposed work is to determine the environmental impact of the disposal of residues from the fluidized-bed combustion of high sulfur coal, and fluidized-bed gasification of high sulfur residual oil. The specific objectives to be achieved are to determine:

1. The characteristics of the solid, sludge, and liquid residues from the fluidized-bed processes applied to coal and oil.
2. The leachate constituents and quantities from land and ocean site disposal of the residues.
3. Other potential environmental effects from disposing the residues into alternative land and water sites.
4. The potential for utilizing solid residues for manufacture of commercial products and for other purposes.
5. Pretreatment requirements for the residues, prior to their disposal.

Discussion

Literature reviews, laboratory tests, and field studies are being used to determine the environmental impacts of disposal of solid and liquid residues from fluidized-bed operations. Residues from fluidized-bed combustion of high-sulfur coal and fluidized-bed gasification of high-sulfur residual oils are being tested. Residues were obtained from three pilot plants; two are supported by the EPA, and one is supported by ERDA. The three plants are: Pope, Evans, & Robbins-FBM Combustion Laboratory, Alexandria, Virginia, burning Pennsylvania coal; Exxon Research & Engineering Company, Linden, New Jersey, burning Illinois fuel; and Esso Petroleum Company, Limited, Abingdon, Oxon, England, gasifying No. 6 Venezuelan oil.

In general, the literature search provided information on the disposal, reuse, and environmental impacts of similar residues, such as coal ash or SO₂ limestone scrubber wastes. Information on the types of waste residues from these processes summarized in laboratory and pilot test reports has also been obtained. From these sources, estimates were made of the conditions for and the levels of pollutants anticipated from the wastes in various environments. Process descriptions of material flows for the three plants were obtained from the EPA and ERDA authorities. Models of the subject disposal environments were developed from the literature and were used to predict the various natural site conditions. The results of the literature search were used in designing specific test conditions, limits, and goals.

A comprehensive program of residue characterization was initiated to determine the chemical and physical properties of the six residues. The resultant physical property data was used to hydraulically design 36-plus pilot test columns for leachate studies. The resultant chemical property data was used as a baseline for the leachate tests and also to identify constituents for which the test column leachate would be analyzed.

The laboratory studies were used to duplicate, on a small scale, eight disposal environments: coal mine, dolomite and limestone quarries, ocean, sanitary landfill, and sand, clay and silt soils. Environmental variables were controlled to duplicate as many real world conditions as possible that would affect the behavior of the residues in natural environments. All leachate was collected, and analyzed. Precise analytical profiles of the residues and their disposal conditions were established.

Large scale field test programs were postponed when it proved impossible to obtain sufficient quantities of residues. To compensate, an expanded program of pilot scale test columns, laboratory columns, and product testing was initiated. When additional residues became available, the data obtained from the aforementioned studies will be used to design and monitor the large scale field leachate tests.

Studies were undertaken to determine the possibility of recovering and marketing the residues instead of disposing of them. Bench tests investigated using residues in the manufacture of certain commercial products. Work is in progress using residues in soil cement, lime-fly ash-aggregate and lime-fly ash-cement-aggregate mixtures, and as load bearing fill. Tests were completed using residues in concrete and asphalt. These tests compared the properties of the recovered product with that produced using conventional raw materials. A preliminary market study was performed to establish the market potentials for the residues and their finished products.

Concurrent with the product feasibility task, an evaluation of requirements for treating residues was made to see if pretreatment can enhance product use or is required for disposal.

Potential use of the spent residues as soil conditioners for agricultural purposes was investigated. Mixtures of fly ash and bed material with soil have produced a variety of crops (tomato, spinach, lettuce, corn, and sorghum). Acidic soils may contain high levels of aluminum and manganese which are easily soluble and sometimes believed to be toxic to crops; however, it has been known for a long time that an increase in pH will decrease the uptake of heavy metals. Lime is presently used to help increase the pH but the residues would presumably replace the lime.

Continuing Investigations

The work planned for the second and third years includes continuing the following: long-term leaching in the 36 test columns, and completion of product testing of residue use as a cement substitute and as a soil conditioner.

CHAPTER 3

PRELIMINARY RESULTS

The fly ash and fluidized-bed residue materials used in the study were from pilot plants operated by Exxon, Linden, New Jersey; Pope, Evans, and Robbins, Alexandria, Virginia; and Esso, in England. For brevity they are referred to in this chapter as Exxon, PER, and Esso.

The following results are based on partial information and may change when the work, which is still in progress, is completed:

1. A comprehensive review of literature indicated that no historical environmental data existed on coal fluidized-bed combustion and oil gasification, other than progress reports on the various pilot plants and technologies currently under development.
2. No full-scale commercial fluidized-bed power plant is at present operating in the world.
3. Extensive literature describing conventional coal and oil combustion residue, physical and chemical characteristics, their ultimate disposal, and recovery alternatives was found. Similarly, considerable literature on lime and magnesium sludge residues and their reuse in various applications was found.
4. The literature review and data developed from over 200 different sources during the first year for this project report indicated the following differences between fly ash from fluidized-bed combustion and conventional coal and oil-fired combustion:
 - Residues from fluidized-bed combustion (FBC) are derived from spent stone and fly ash, and differ from conventional coal combustion dolomite or lime scrubber sludges and fly/bottom ashes.
 - Fluidized-bed combustion normally produces solid residues, whereas conventional combustion scrubbers produce liquid sludges as well as some bottom ash solids.
 - Test fluidized-bed fly and bottom ash samples were dry, whereas conventional combustion plant ashes are wetted to quench burning coals and to cool the residues.
 - The FBC residue samples had higher specific gravities (weights) than conventional fly ash, and thus would not be as suitable for use in lightweight concrete and structural fills.
 - The FBC fly/bed test residues had been recirculated and hence contain less organic material compared to conventional unrecirculated residues.

5. Results of laboratory mixing/leaching tests for residue characterization showed water soluble fractions in Exxon fly ash were higher than acid soluble fractions for boron and magnesium, and higher than base soluble fractions for nitrate. Water soluble fractions in Exxon spent bed material were higher than acid soluble fractions for sulfate, boron, lead, magnesium, and sodium, and higher than base soluble fractions for nitrate, aluminum, calcium, copper, manganese, and molybdenum.

Water soluble fractions in PER fly ash were higher than acid soluble fractions for sulfate, boron, lead, and sodium, and higher than base soluble fractions for nitrate, calcium, copper, magnesium, manganese, molybdenum, and nickel. For PER spent bed materials, the water soluble fractions exceeded acid soluble fractions for sulfate, boron, and sodium, and exceeded base soluble fractions for nitrate, aluminum, boron, calcium, copper, magnesium, manganese, and molybdenum.

All the constituents in the Esso fly ash except chloride, nitrate, and phosphate were less in the water soluble fraction than in the acid soluble fractions. The water soluble fraction exceeded the base soluble fraction for chloride, nitrate, phosphate, aluminum, calcium, chromium, iron, lead, manganese, mercury, molybdenum, silver, and zinc ions. For the Esso spent bed material, the acid soluble fractions exceeded the water soluble fractions for all the constituents except sulfate, boron, mercury, and molybdenum, and the water soluble fractions exceeded the base soluble fractions for all the constituents except sulfate, aluminum, arsenic, beryllium, magnesium, and zinc.

Cyclone fly ash water soluble fractions were less than acid soluble fractions for all constituents and exceeded base soluble fractions for nitrate, aluminum, calcium, iron, magnesium, manganese, molybdenum, silver, and zinc. Esso fines, stack fly ash water soluble fractions exceeded acid soluble fractions for chloride, boron, and molybdenum, and exceeded base soluble fractions for nitrate, arsenic, boron, cadmium, calcium, iron, lead, magnesium, molybdenum, and silver. Due to a shortage of residues for analysis, some acid and base soluble fractions were not determined.

6. BOD tests to determine the biochemical rate of decomposition of residue water soluble extracts in a standard solution of glucose and peptones were compared with a control standard solution. The solutions with added residues showed a lag time of two days during which BOD was inhibited, and the BOD increased so that the 5-day oxygen demand samples were nearly as high as the control sample. The results indicated that the leachates contain constituents which can act as temporary inhibitors to microorganism growth in the wastewater containing biodegradable organic compounds.

7. Laboratory bench-scale leaching tests run in 6 1/2 cm diameter x 21 cm length vessels to evaluate column strata granular materials indicated the following principle dissolved constituents:

- Granite bedrock: sulfate, sodium, and traces of arsenic.
- Bituminous coal: sulfate, arsenic, calcium, and sodium.

- Dolomite: sulfate, arsenic, sodium, and traces of boron and potassium.
- Limestone: sulfate, sodium and traces of arsenic, cadmium, potassium and lead.
- Silica sand (number 60): sulfate, sodium, chloride, and traces of potassium.
- Silica sand (number 16): sulfate, sodium, chloride, potassium, and traces of magnesium, lead and calcium.
- Claystone: sulfate, sodium, arsenic, chloride, and traces of calcium, lead, and magnesium.

8. High rate leaching tests were developed for the laboratory bench-scale residue vessels and provided the following principle dissolved constituents:

- Fluidized bed sample residues leached sulfate and chloride anions, and calcium, magnesium, iron, sodium, and potassium cations in significant concentrations. Many trace elements were also leached in relatively low concentrations.
- Chloride, sodium, and potassium were nearly completely extracted from the sample residues after six times the residues' weight in water had leached through the residue.
- Calcium and sulfate were leached at relatively constant high concentrations after residues had received six times their weight in water.
- Residue leachate contained nickel, lead and iron compounds concentrations exceeding the U.S. EPA recommended permissible levels for drinking water supplies.
- Sulfate content in the residue leachate exceeded the noted recommended standard. However, sulfate may combine with calcium to form gypsum, or with lead to form lead sulfate. Both of these sulfate compounds are relatively insoluble and thus will reduce the leaching of calcium and lead.
- Acid water increased the leaching of heavy metals.

9. Cation exchange capacities (CEC) of the Esso and Exxon spent bed materials were equal at 1.9 CEC meq per 100 grams of residue. PER fly ash and spent bed materials were 2.4 CEC meq per 100 grams of residue. Exxon fly ash was 0.5 and Esso fly ash was 13.6 CEC meq per 100 grams of residue.

10. Acid neutralization capacities varied from 2.6 equivalents per kg for PER spent bed material to 78.1 for Esso fly ash, probably due to different ratios of calcium to sulfur in these materials, as received.

11. Exothermal reactions occurred after wetting all of the "as received" residues except Exxon fly ash. The exothermal reactions were attributed largely to lime slaking upon addition of water. Residue slaking temperatures were measured as high as 240°C (Exxon spent bed material).

12. The fluidized bed fly ash particle sizes were fine (similar to a type of sandy silt) and the composition was unchanged by slaking. The spent bed material particle sizes, as received,

were similar to sand and became even finer after slaking. Oil gasification residue particle analyses fell within a narrow band corresponding to a typical sand with fines. The exception was unslaked Esso spent bed materials whose particle size distribution corresponded to a typical sand.

13. The specific gravity values for Exxon and PER fly ashes (2.6 - 2.8) were in the range for normal soils. Esso fly ash specific gravity at 2.02 was less than for normal soils. The spent bed residues partly entered into solution after water was added; thus, their specific gravity was difficult to determine accurately.

14. The residues "as received" had zero moisture content.

15. Water addition will likely change the dry densities of all the residues tested except the PER fly ash. Esso residue densities decreased significantly in dry density (by 37 - 49 percent dry weight) and Exxon spent bed material increased significantly (by 48 percent) after water addition.

16. The ability of dry residues to hold moisture, termed their water holding capacity, ranges between 0.44 and 0.98 grams of water per gram of dry sample.

17. Pilot test column simulation indicated that the residue leachate had the following characteristics:

- A highly alkaline leachate resulted from coal mine, dolomite quarry, limestone quarry, and ocean environments.
- A neutral leachate resulted from the landfill environments due to the neutralization of alkaline residue leachate by acidic landfill leachate.
- High initial peak concentrations of sulfate occurred in all environments.
- Soluble chlorides in residues were readily leached without attenuation in all of the column strata materials.
- Concentrations of mercury in sea water leachate may be an order of magnitude higher than concentrations found in leachate from other land-type conditions.
- Sea water leached iron from the residues more rapidly than fresh water did.
- Slight attenuation of zinc in residue leachate may occur in the column strata.
- Total dissolved solids were leached in decreasing quantities with the increasing passage of water.

18. Residues can be used as a conditioner for soils that are acidic, high in heavy metals, or deficient in trace metals. Residues are a marketable source of calcium or magnesium and are a substitute for lime or gypsum to raise soil pH.

19. Substitution of residues in portland cement concrete mixtures could save about \$0.50 per kkg of equivalent strength concrete.

CHAPTER 4

FLUIDIZED-BED COAL COMBUSTION

Introduction

In fluidized-bed combustion, a granulated bed material (limestone or dolomite) encompasses the pulverized burning coal. The bed and fuel are fluidized by combustion air. The calcareous bed materials absorb sulfur oxides, reducing their emission into the environment. The process generates large quantities of dolomite or limestone materials, magnesium or calcium sulfate, ash and some unburned coal. This sorbent material may be either re-generated for repeated SO_x removal, or removed from the plant for disposal.

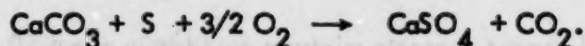
There have been two approaches to steam generation using fluidized-bed boilers. One method uses direct contact between the inert fluidized, heated stone particle bed and the heat transfer surfaces (boiler tubes) to produce steam. An example of a fluidized-bed steam generator with direct contact heat transfer is shown in Figure 1. The hot flue gas, after ash removal, can generate additional heat. In boilers without direct fluidized-bed contact, hot off-gases generate all the steam by conventional fashion.

The start-up of an atmospheric fluidized-bed boiler requires heating a portion of the bed to 400°C to ignite the injected coal. After ignition, the temperature of the bed rises until the energy released in the bed equals the energy absorbed by the boiler tubes plus that in the hot gases leaving the bed, and the system achieves thermal equilibrium. Excellent heat transfer and high heat capacity is maintained in a fluidized-bed boiler at uniform temperature, typically in the range of 800 to 900°C .

High heat-transfer coefficients between the fluidized-bed and immersed steam generation surfaces reduce the steam tubing requirements, and also permit operation at lower and more uniform bed temperatures. The lower temperatures reduce NO_x emissions and slag, and decrease equipment corrosion.

Process Descriptions

There are two fluidized-bed combustion modes, with either complete or partial combustion of the fuel. In the complete combustion mode (also called one-step or excess oxygen combustion), oxygen in excess of the stoichiometric quantity required to burn the fuel is fed to the fluidized bed. The oxygen reacts with sulfur, forming sulfur dioxide, which in turn reacts with the calcium or magnesium in limestone or dolomite (hereafter simplified to refer only to the calcium):



In the second mode (called two-step or oxygen deficient combustion), less than the stoichiometric amount of oxygen is added to the fluidized bed. This results in the formation of calcium sulfide (CaS) which can be converted to SO_2 and CaO by roasting it in air or in

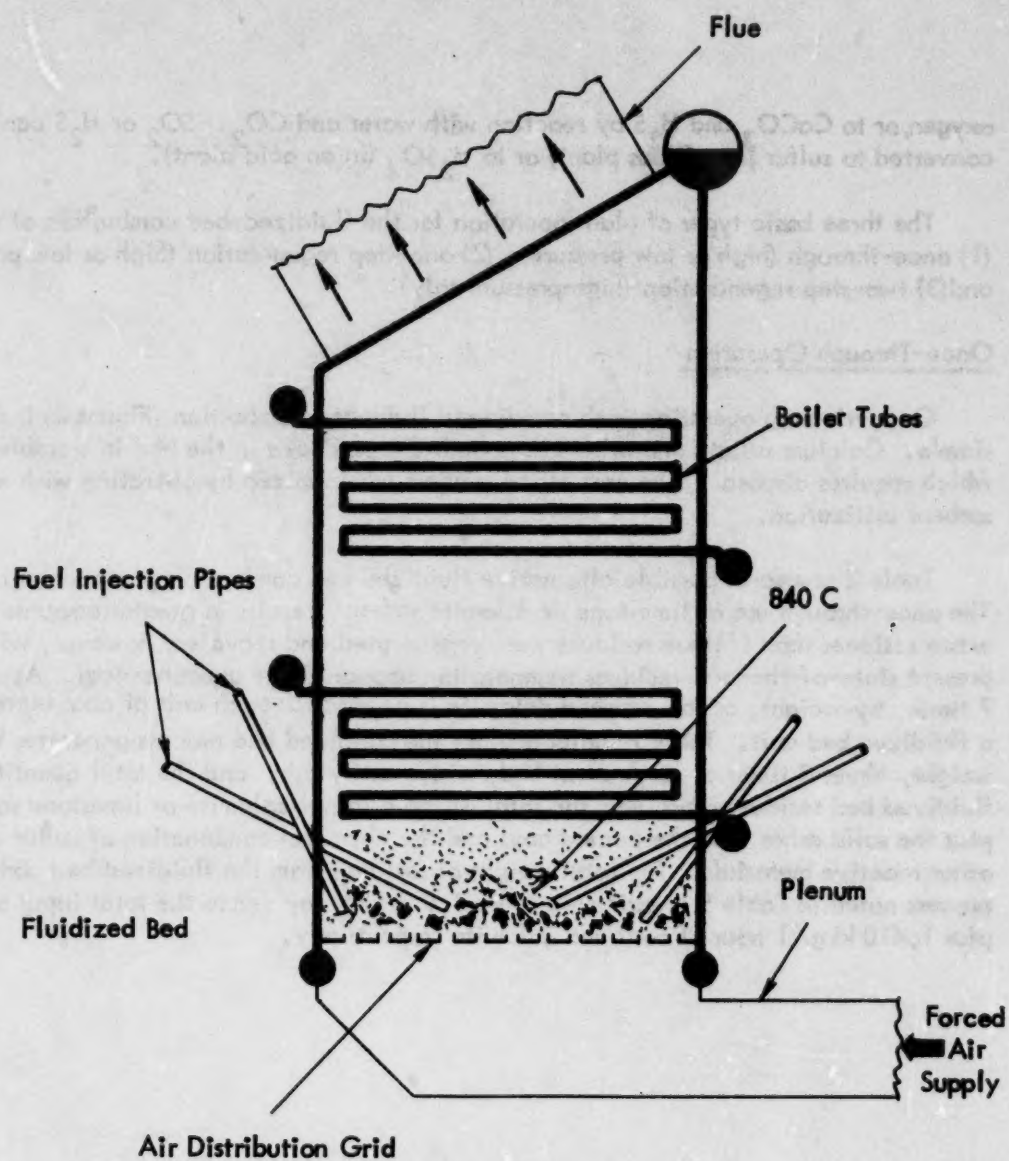


Figure 1. Direct contact fluidized-bed steam generator.

Source: 104.

oxygen, or to CaCO_3 and H_2S by reaction with water and CO_2 . SO_2 or H_2S can be converted to sulfur (in a Claus plant) or to H_2SO_4 (in an acid plant).

The three basic types of plant operation for the fluidized-bed combustion of coal are: (1) once-through (high or low pressure), (2) one-step regeneration (high or low pressure), and (3) two-step regeneration (high-pressure only).

Once-Through Operation

Once-through operation with pressurized fluid-bed combustion (Figure 2) is quite simple. Calcium sulfate and other compounds are produced in the bed in a stable form which requires disposal. The cost of the process is minimized by operating with maximum sorbent utilization.

Table 7 compares possible alternative fluidized bed combustion plant sorbent processes. The once-through use of limestone or dolomite sorbent results in greater amounts of waste residues than if these residues were regenerated and recycled; however, with the present state-of-the-art, residues regeneration appears to be uneconomical. Approximately 7 times, by-weight, of raw crushed dolomite is needed for each unit of coal burned in a fluidized bed unit. Table 7 indicates that the fluidized bed process generates, by weight, about 3 times as much spent bed residue as fly ash, and the total quantity of fluidized bed residues represents the total of the original dolomite or limestone sorbent plus the solid ashes from the burned coal and the chemical combination of sulfur and other reactive materials. The total weight of residues from the fluidized bed combustion process noted in Table 9 is estimated to be 1,958 kkg/day versus the total input of 195 plus 1,410 kkg/1 hour of coal and dolomite respectively.

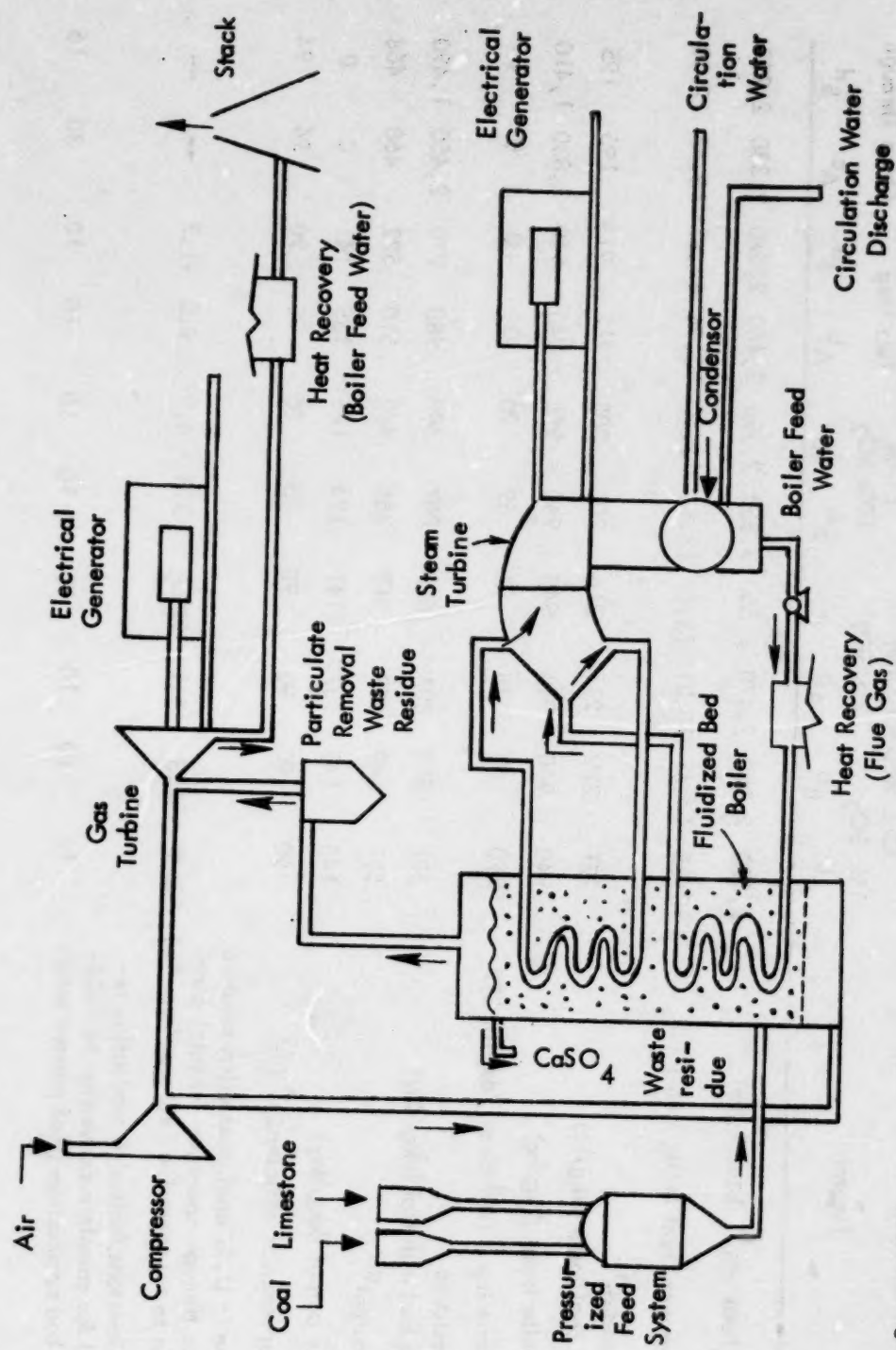


Figure 2. Once-through pressurized fluidized bed boiler power plant.

Source: 104.

TABLE 7. COMPARISON OF FBC SORBENT PROCESSES

TABLE 7. COMPARISON OF FBC SORBENT PROCESSES																	
Impact	One Step - 10 atm						One Step - 1 atm		Two Step		Once Through						
	1% SO ₂		2% SO ₂		10% SO ₂		10% SO ₂		A ^b B ^b		A ^c B ^d						
Energy																	
Plant heat rate ^e (kcal/kwhr)	2,600	2,700	2,470	2,550	2,360	2,390	2,460	2,520	2,330	2,290							
Plant energy cost (mills/kwhr)	13.88	14.61	13.21	13.67	13.13	13.59	13.94	14.67	13.45	12.30							
Raw materials ^f																	
Total coal input (kkg/hr)	221	229	211	216	202	205	212	218	195	195							
Dolomite input (kkg/hr)	940	940	940	940	940	940	940	940	2,830	1,410							
Methane input (10 ³ cu m /day) at STP	790	103	75	97	69	90	0	0	0	0							
Plant residues																	
Spent bed material (kkg/day)	807	698	807	698	807	698	980	970	2,450	1,490							
Ash output ^g	531	549	508	518	485	492	510	522	468	468							
Sulfur output (kkg/day)	143	149	137	141	124	125	139	141	0	0							
Sulfur removal efficiency ^h (%)	90	90	90	90	85	85	90	90	94	94							
Increase in U.S. coal production relative to once through operation for total conversion to regenerative FBC processes (%)	13.3	17.3	8.1	10.5	3.8	4.9	9.0	11.7	--	--							
U.S. limestone/dolomite production required for complete conversion to fluidized bed combustion (% of present total)	10	10	10	10	10	10	10	10	30	15							

(continued)

TABLE 7 (Cont.)

- ^a Bases for analysis:
 195,000 kg/hr coal feed to boilers
 4.6% sulfur by weight in coal
 boiler sulfur removal efficiency = 95%
 dolomite utilization in boiler = 30% (regenerative systems)
 dolomite utilization after regeneration = 10%
 dolomite make up rate = 1 mole Ca/mole S (regenerative systems)
 dolomite cost = \$11/kg
 coal at \$1.79/10⁶ kcal
 methane at \$3.17/10⁶ kcal
 sulfur recovery efficiency = 90%
- ^b Column A for disposal before regeneration, Column B for disposal after regeneration.
- ^c At 3.0 moles Ca/mole S dolomite make up rate and 31.6% utilization in boiler.
- ^d At 1.5 moles Ca/mole S dolomite make up rate and 63.3% utilization in boiler.
- ^e Includes methane input.
- ^f Other materials for regeneration processes include process water, chemicals, and catalysts.
- ^g 10% ash in coal.
- ^h Sulfur removal efficiency is lower for the one-step process at 1 atmosphere pressure because the process tail gas is incinerated rather than recycled to the boiler.

CHAPTER 5

RESIDUE CHARACTERIZATION

Purpose

The purpose of this subtask was to determine the chemical and physical properties of FBC residue samples and the materials used in pilot-scale column studies. This provided a preliminary screening of potential environmental effects and direction of subsequent efforts. Results were used in planning and conducting the pilot-scale column studies of residue disposal, and in testing residue commercial and agricultural applications.

Residue Characteristics

The chemical composition of ash and spent bed material is dictated, to a large extent, by the composition of the bed material and the fuel. Natural materials are largely impure, and both coal and oil as well as limestone and dolomite contain traces of most metals. Concentrations will vary depending on local sources. Combustion and other high temperature reactions produce ashes and spent bed material containing many of these trace metals. The specific chemical composition of a given ash or spent bed material is dependent on the combustion parameters, the fuel, and the bed material; and as a result, the composition of ash and bed material varies widely.

All of the residue samples available to us were from the pilot plant test runs and may not be representative of future production runs. Where possible, we have attempted to determine the actual pilot plant test operating conditions and acquired analyses of the raw fuel and sorbent feeds. Given this latter information, it should be possible to relate our test results to future production conditions. Table 8 lists the residues analyzed in the laboratory and their test run conditions.

Tables 9 through 11 give available analyses of coal and limestone feeds provided by some of the experimental plants. The composition of fossil fuels used in these experiments varied widely. The percentages of sulfur in the coal ranged from 0.75 to 4.46, and in the coke about 1.28 (on a dry basis). Venezuelan No. 6 oil was used in the Esso gasifier; and the sulfur content was about 2.5 percent. Unfortunately, not all the experimental plants providing residues were able to provide complete chemical analysis or other descriptive information about the raw materials that were used.

The composition of the limestone used for the fluidized-bed combustion tests varied. The percentage of calcium in the PER limestone was 36, and 47.5 for Greer and Germany Valley, respectively. Available data showed that the sulfur content of the limestones was 0.3 percent for Greer and 0.15 percent for the Germany Valley limestones. Magnesium, iron, aluminum and silicon were other important constituents in the limestones. Probably both limestone and coal contained several trace metals, but available data showed only Titanium (0.89 percent in the coal used for the PER plant).

TABLE 8. PILOT PLANT OPERATION FOR CHARACTERIZED RESIDUES

Residue Source	Run No.	Temp. °C	Excess Air Vol. %	Fuel Type	Sulfur %	Bed Sorbent	Ca/S molar feed ratio	Flue SO ₂ ppm
Pope, Evans & Robbins Alexandria, Va. Fly ash Spent bed material	N.A. [*]	815 to 870	18	High sulfur bituminous coal Sewickley, Pa.	4 to 4.5	Calced limestone Germany Valley & Greer, W. Va.	Variable	Variable
Exxon Miniplant Linden, N. J. Fly ash Spent bed material	30.4	835 (avg.)	16.1	Illinois No. 6	4.2 to 4.8	Grove limestone	3.7	894
Esso CAFB Abingdon, England Cyclone fly ash Fines, stack fly ash Spent bed material	10	860 to 950	N.A. ^a	No. 2 heating oil Venezuela	2.5	Lime BCR1359 U.S.A.	1 (avg.)	200

^a N. A. = Not Available.

TABLE 9. CHARACTERIZATION OF POPE, EVANS, AND ROBBINS
BITUMINOUS COAL SAMPLES (percentage by weight)

Constituent	Coal	Coke *	Ash
Ash	17.44	27.82	100.0
Volatiles	37.31	0.00	0.0
Fixed carbon	45.25	72.18	0.0
	<u>100.00</u>	<u>100.00</u>	<u>100.0</u>
Pyritic sulfur	3.04	0.00	0.0
Sulfate sulfur	0.18	0.29	1.0
Organic sulfur	1.24	0.99	0.0
Total sulfur	<u>4.46</u>	<u>1.28</u>	<u>1.0</u>
Carbon	67.56	76.18	0.0
Hydrogen	4.80	0.00	0.0
Nitrogen	0.93	0.00	0.0
Sulfur	4.46	1.28	1.0
Silicon	4.08	6.51	23.4
Iron	2.48	3.96	14.2
Aluminum	1.80	2.87	10.3
Calcium	0.63	1.00	3.6
Magnesium	0.10	0.16	0.6
Potassium	0.38	0.61	2.2
Sodium	0.10	0.16	0.6
Titanium	0.09	0.14	0.5
Oxygen	12.59	11.3	43.6
	<u>100.00</u>	<u>100.00</u>	<u>100.0</u>

* Calculated values.

Source: 186.

TABLE 10. CHARACTERIZATION OF POPE, EVANS, AND ROBBINS
LIMESTONE SAMPLES (percentage by weight)

Constituent	Greer Limestone	Germany Valley Limestone
Calcium carbonate (CaCO_3)	75.0	98.3
Magnesium carbonate (MgCO_3)	4.0	0.5
Ferric oxide (Fe_2O_3)	0.75	0.2
Alumina (Al_2O_3)	3.3	0.5
Silica (SiO_2)	9.5	0.6
Sulfur (S)	0.3	0.15

Source: 186.

TABLE 11. CHARACTERIZATION OF EXXON MINIPLANT COAL SAMPLES
(percentage by weight)

Constituent	As Analyzed	Dry	After Ignition
Moisture	3.3	--	--
Ash	9.95	10.26	--
Volatiles	10.00	10.31	--
Carbon	67.71	69.81	77.79
Hydrogen	4.77	4.92	5.48
Nitrogen	1.17	1.21	1.34
Oxygen	9.19	9.47	10.55
Chlorine	0.05	0.05	0.06
Sulfur	4.20	4.33	4.83

Source: 187.

Chemical Composition

The preliminary chemical tests of the residue samples consisted of: 1) characterization after hydrofluoric acid digestion; 2) determination of their water, basic, and acid soluble fractions, and 3) determination of their sequential water leaching characteristics.

Total Residue Characterization. The total chemical compositions of the residue samples were determined after hydrofluoric acid digestion placed appropriate constituents into solution. One gram residue samples were digested according to the procedure outlined in the American Society of Agronomy's Methods of Soil Analysis, 1965, p. 1019. The only significant departure from this procedure was the use of nickel instead of platinum utensils; therefore, total nickel analysis was not performed. The digestate was diluted to 100 ml. All analyses of the digestate were conducted according to EPA Methods for Chemical Analysis of Water and Wastes and Standard Methods, (14th ed.). Appendix A of this report gives methods and references for each analysis. Analytical results are presented, hereinafter, in the report.

Soluble Fraction Analysis. The solutions to be analyzed were prepared by placing 100 g samples of each type of residue, as received, in a flask and adding either 250 ml of distilled water, 1.0 N NaOH, or 1.0 N HNO₃ in accordance with EPA recommended procedures as further described in Appendix A. After mixing for twenty-four hours, the solutions were filtered and the filtrate analyzed to determine the acid, base and water soluble fractions of the residues, as well as pH, COD, BOD, and TDS. All analyses were conducted as for the total characterization procedure, and are cited in Appendix A.

The BOD₅ analyses were performed on the water extracts and on distilled water samples. The extract and distilled water samples contained 6.5 percent of a nutrient solution of glucose, peptone, calcium chloride, magnesium sulfate, ammonium chloride, sodium phosphate, potassium phosphate, and ferric chloride.

Bench-Scale Leaching Tests. Preliminary bench-scale leaching tests were conducted on residue samples prior to the construction of the pilot-scale test columns. The purpose of these tests was to estimate the long-term leaching characteristics of the residues. Two hundred and fifty gram samples of each residue were placed in 30.48-cm high, 5.08-cm ID plastic columns. Figure 3 illustrates the column operations. The water was added at the rate of 250 ml per leaching cycle. Leachate was collected by gravity percolation once a week for six weeks. Analyses were performed on the leachate by the methods indicated in Appendix A.

Laboratory-scale leaching studies were also conducted on the various stratal materials used in the large-scale test columns. Table 12 lists the types and quantities of materials tested. Three 250 ml leaching cycles were done using the procedures described above. Chemical analyses were conducted to determine the quantities of various constituents leached out of these materials over time. These values were then used to help establish background or baseline concentrations of leachate constituents analyzed in the pilot-scale columns. Accelerated small-scale column leaching was also developed to simulate 52



Figure 3. Laboratory-scale column leaching.

TABLE 12. STRATIGRAPHIC MATERIALS SIMULATED IN LEACHING TESTS

Stratigraphic Unit	Simulant Material	Quantity (g)
Sandstone	#16 Silica sand	300
Sandstone	#60 Silica sand	300
Claystone	#60 Silica sand clayr. (kaolin)	240 60
Dolomite	Coarse meal grade dolomite	300
Limestone	Coarse meal grade limestone	300
Granite bedrock	Granitic pea - gravel	225
	Decomposed granite	75
Bituminous coal	Coarse ground lump bituminous coal	100

separate 250 ml leaching cycles in a period of several weeks. The results of these tests were not available at the time that this interim report was prepared.

Chemical Properties Tests

Cation Exchange Capacity

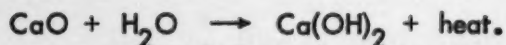
The cation exchange capacities of the residues and column materials were measured to indicate the amount of interchange that could occur as a result of leachate water moving through the various solids in the test columns. The existing cations were replaced with sodium ions in an acetate solution. The sodium ions were then replaced by ammonium ions in the acetate solution. The concentration of sodium ions in the ammonium acetate was measured next and converted to cation exchange capacity in milliequivalents per 100 g of original dry material. A detailed outline of the procedure is given in Appendix A. The residue cation exchange capacity data are shown in Table 13.

Acid Neutralization Capacity

The test involved dissolving a weighted amount of residue in distilled, deionized water. As measured quantities of 12N HCL were added, the pH was monitored until the neutral value was reached. The results were calculated to equivalents of 1 N HCL required to neutralize one kg of residue. These results are presented in Table 14.

Heat Release

One feature of some of the pilot plant residues, as received, has been their extreme exothermal activity upon addition of water. The apparent cause was lime slaking:



Slaking of the sodium, potassium and magnesium oxides also probably contribute some heat release, as well. Temperature changes were recorded for the addition of 3.8 l water to 13.6 kg, and are shown in Figures 4 and 5.

Physical Properties

Residue Preparation

Residue samples to be slaked were covered with water and allowed to react. When all activity had ceased, the slaked samples were dried in an oven at approximately 103° C for 24 hours. Unslaked residue samples were used as received without further drying, since moisture content was already about zero.

TABLE 13. RESIDUE AND COLUMN MATERIAL CATION EXCHANGE CAPACITY

Material ^a	CEC meq/100g residue
EFA	13.6
ESBM	1.9
VFA	2.4
VSBM	2.4
NJFA	0.5
NJSBM	1.9
Limestone	0.6
Dolomite	1.9
Bituminous Coal	2.7
Claystone/Sand, 4:1	7.2
Decomposed Granite	26.6
#16 Silica Sand	1.4
#60 Silica Sand	2.8

^aResidues were slaked before determining CEC.

TABLE 14. RESIDUE ACID NEUTRALIZATION CAPACITY

Source	Residue Type	Neutralization Capacity (equivalents/kg)
Exxon Miniplant	Fly Ash	17.5
	Spent Bed Material	26.0
Pope, Evans, and Robbins	Fly Ash	8.8
	Spent Bed Material	2.6
Esso, England	Fly Ash	78.1
	Spent Bed Material	35.5

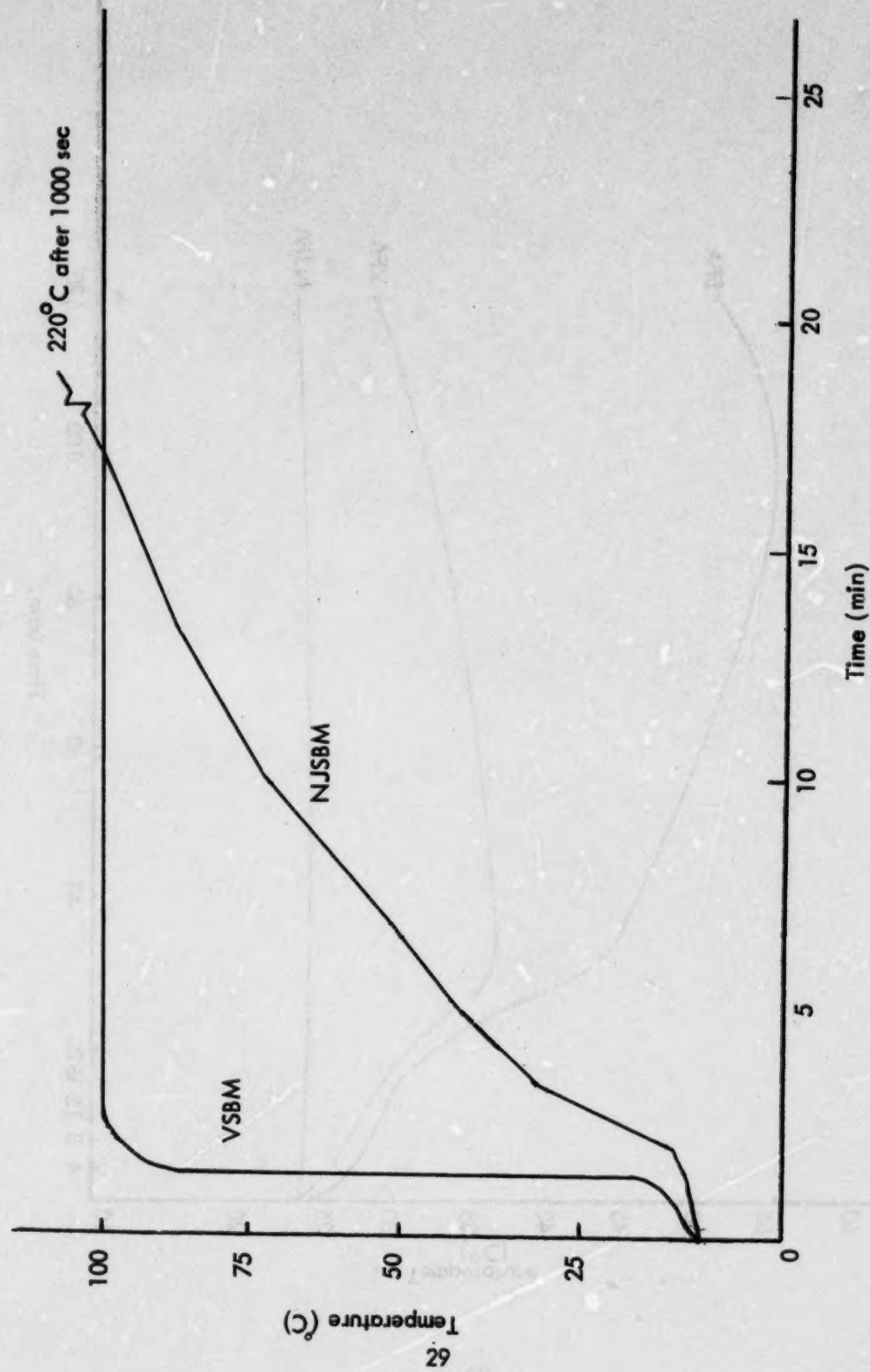


Figure 4. Temperature change from water addition to dry residues.

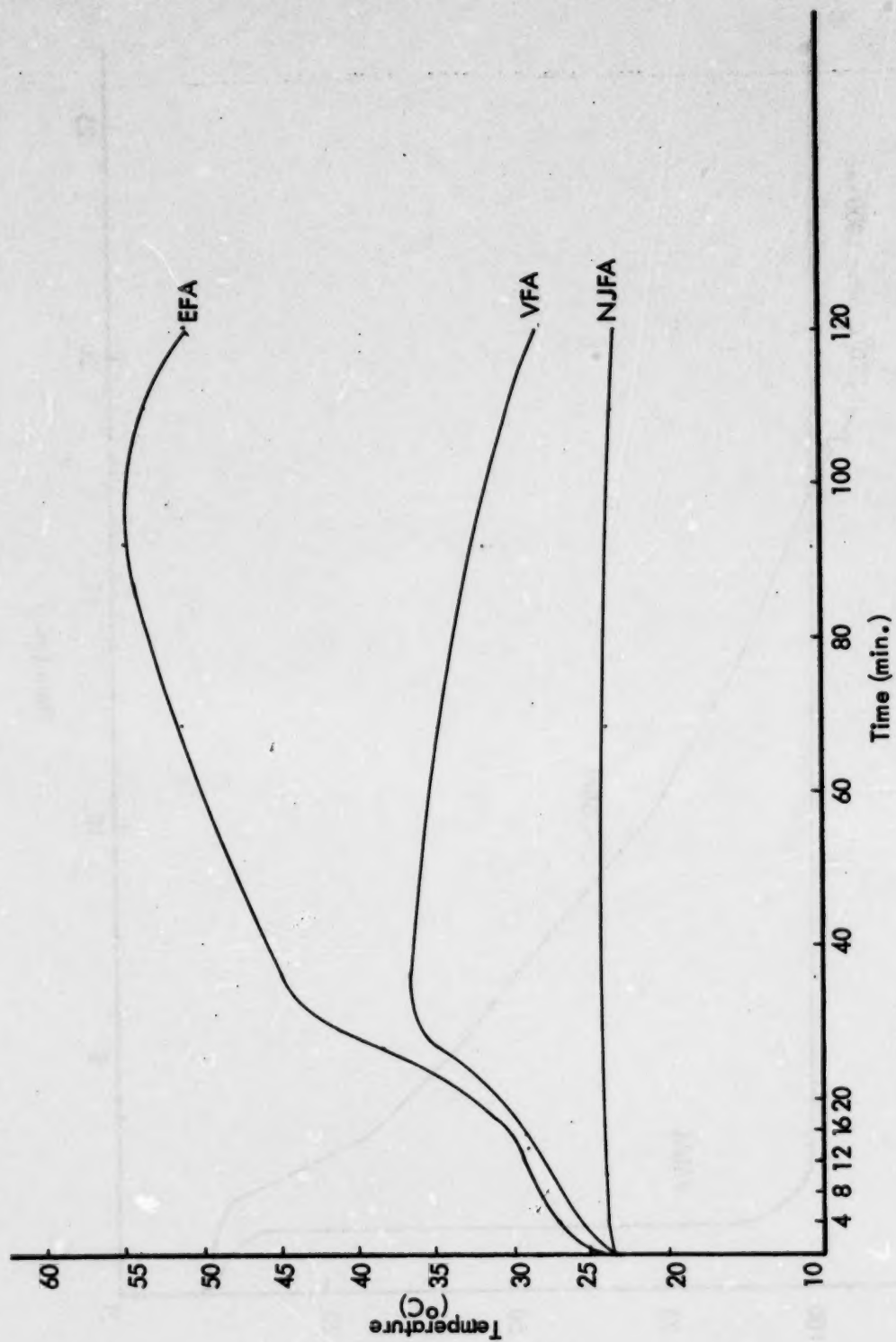


Figure 5 . Temperature change from water addition to dry residues.

Particle Size Analysis

The procedure used complied with ASTM D422. A 500 gm sample of each slaked and unslaked residue was sieved, using the number 4, 10, 20, 40, 80, 100, and 200 sieves. No hydrometer analyses were performed on spent bed materials because some portion of the residue was soluble, which would substantially alter the results. Hydrometer analyses were conducted on slaked samples only for the fly ashes. The results from the hydrometer and the sieve analyses were plotted together, and are presented in Figures 6 and 7. Additionally, the sieve analyses for column strata material are shown in Figures 8 through 10.

Specific Gravity

Specific gravity measurements were made for test residues to establish their physical characteristics for aggregate or other possible uses. The method used was that shown in ASTM D854, except that step 6.2 was changed from a period of partial vacuum to a period of vigorous shaking. This did not affect the results. Specific gravity values were not obtained for the spent bed materials, as some portions were soluble and this phenomenon interfered with the ASTM D854 type analysis.

Moisture Content

Procedures in ASTM D2216 were followed, using the residues as received (see Table 7.).

Degree of Saturation

Degree of saturation was obtained by substituting into the formula:

$$S = \frac{WG}{G \left(\frac{1}{w} / \frac{1}{d} \right) - 1}, \text{ where}$$

W = moisture content

G = specific gravity

Results are shown in Table 7.

$\frac{1}{w}$ = unit weight of water

$\frac{1}{d}$ = unit weight of residue

Loose Dry Density

The dry density of each residue, both slaked and unslaked, was determined by pouring the dried residue into a 100-ml beaker. The difference between the empty and filled weights of the container was divided by the known volume to yield the loose dry density value, which is shown in Table 7.

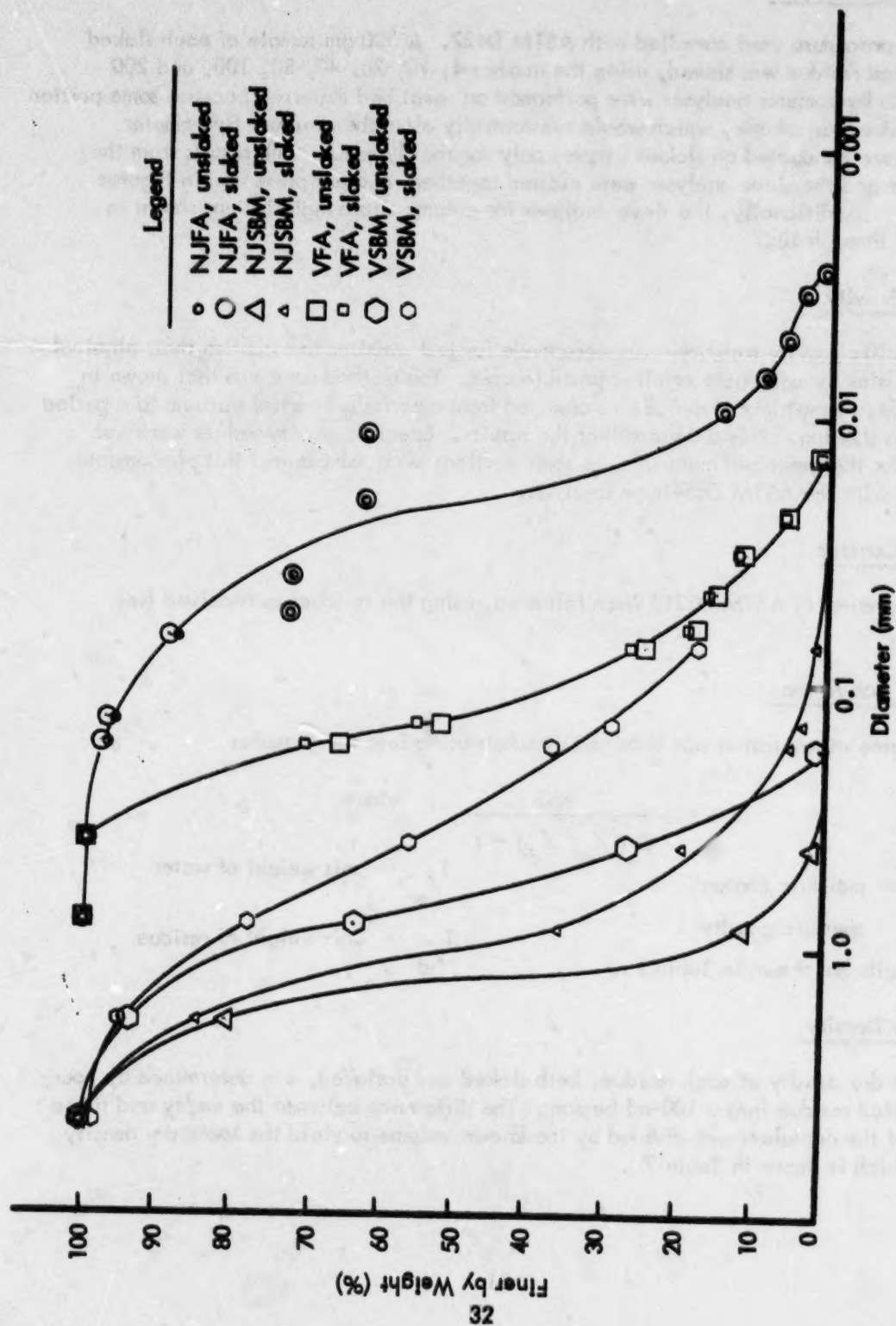


Figure 6 . Particle size analyses: coal combustion residues .

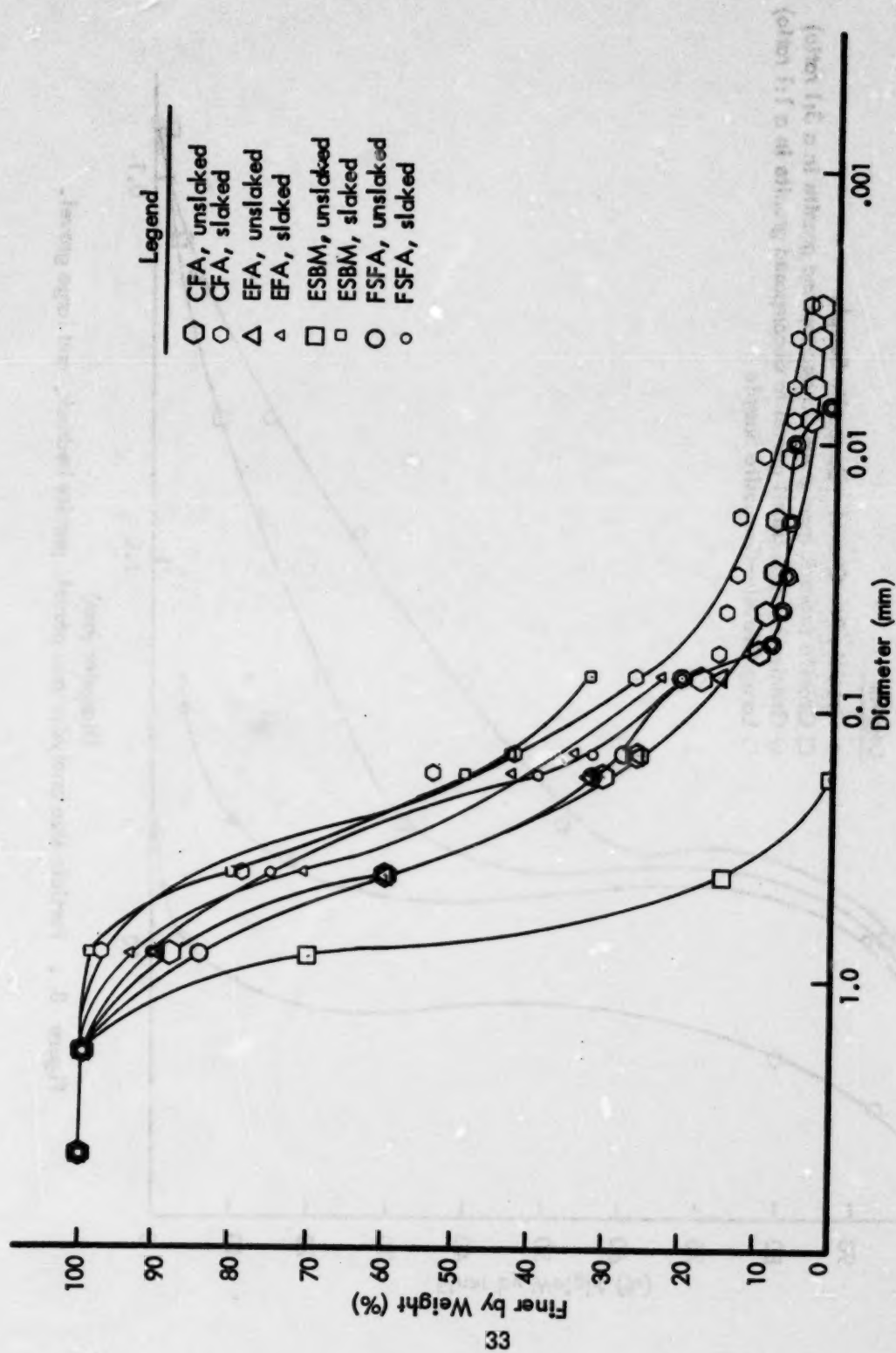


Figure 7 . Particle size analyses : oil gasification residues.

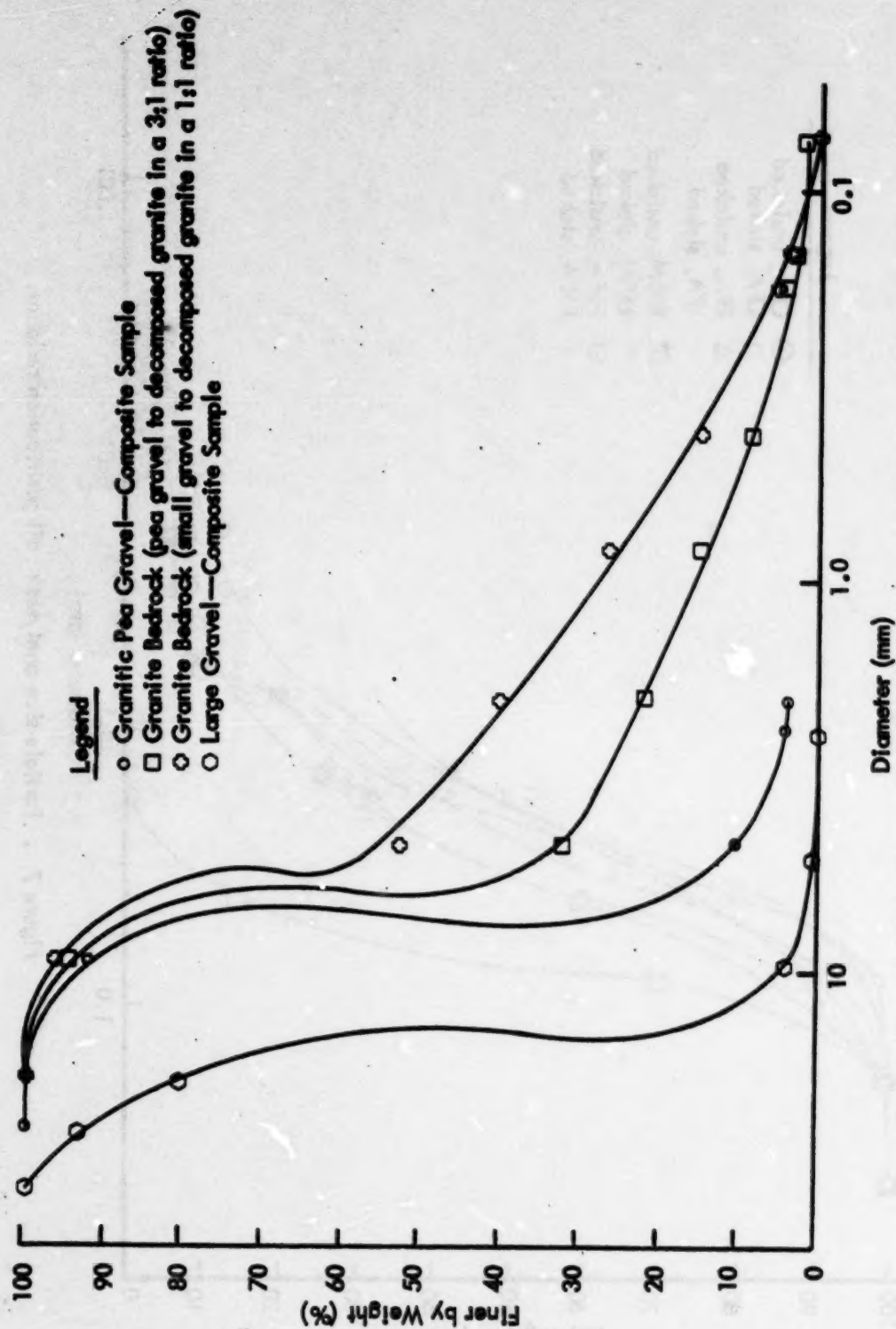


Figure 8. Particle size analysis: pea gravel, granite bedrock, and large gravel.

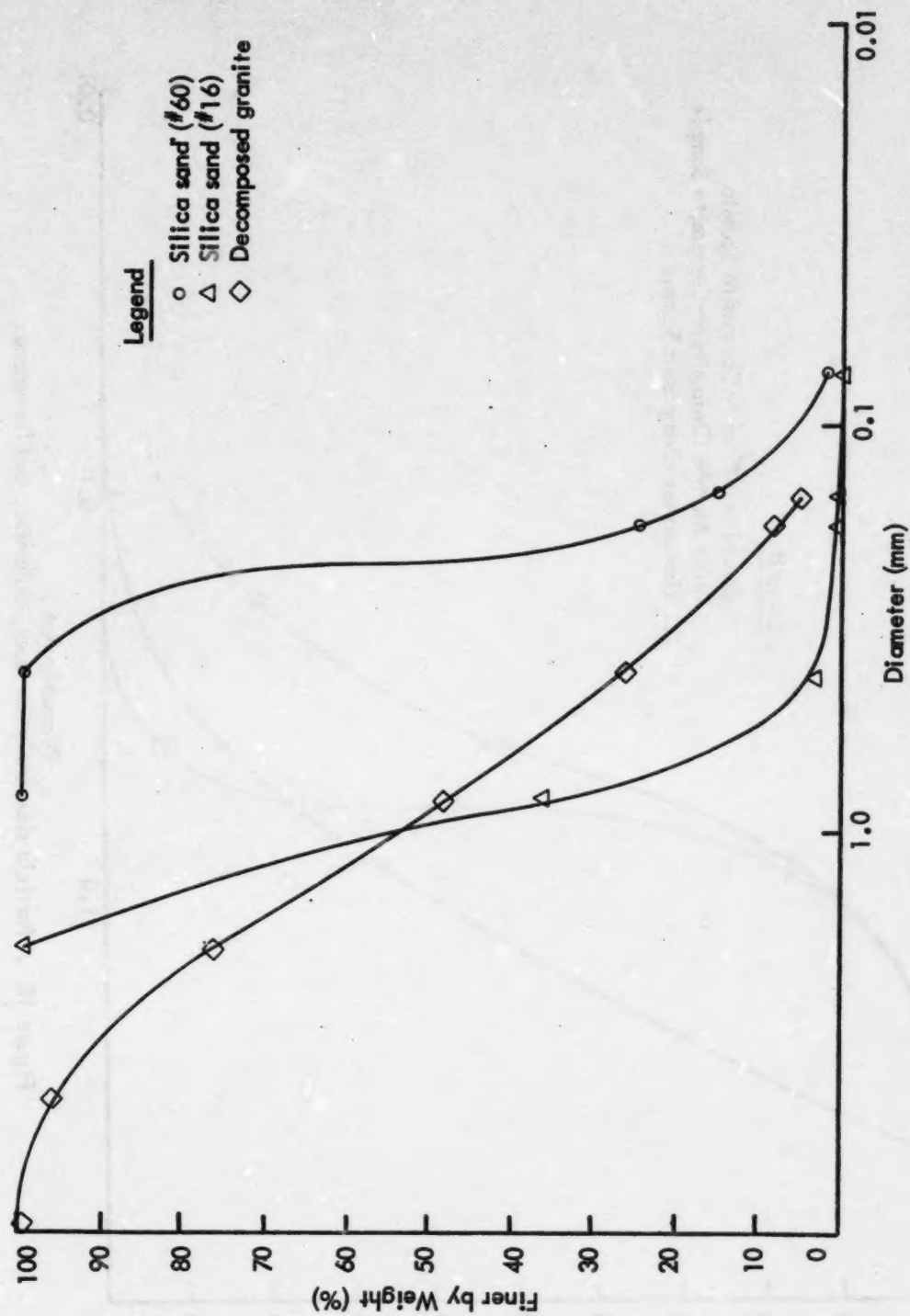


Figure 9 . Particle size analysis:silica sand and decomposed granite .

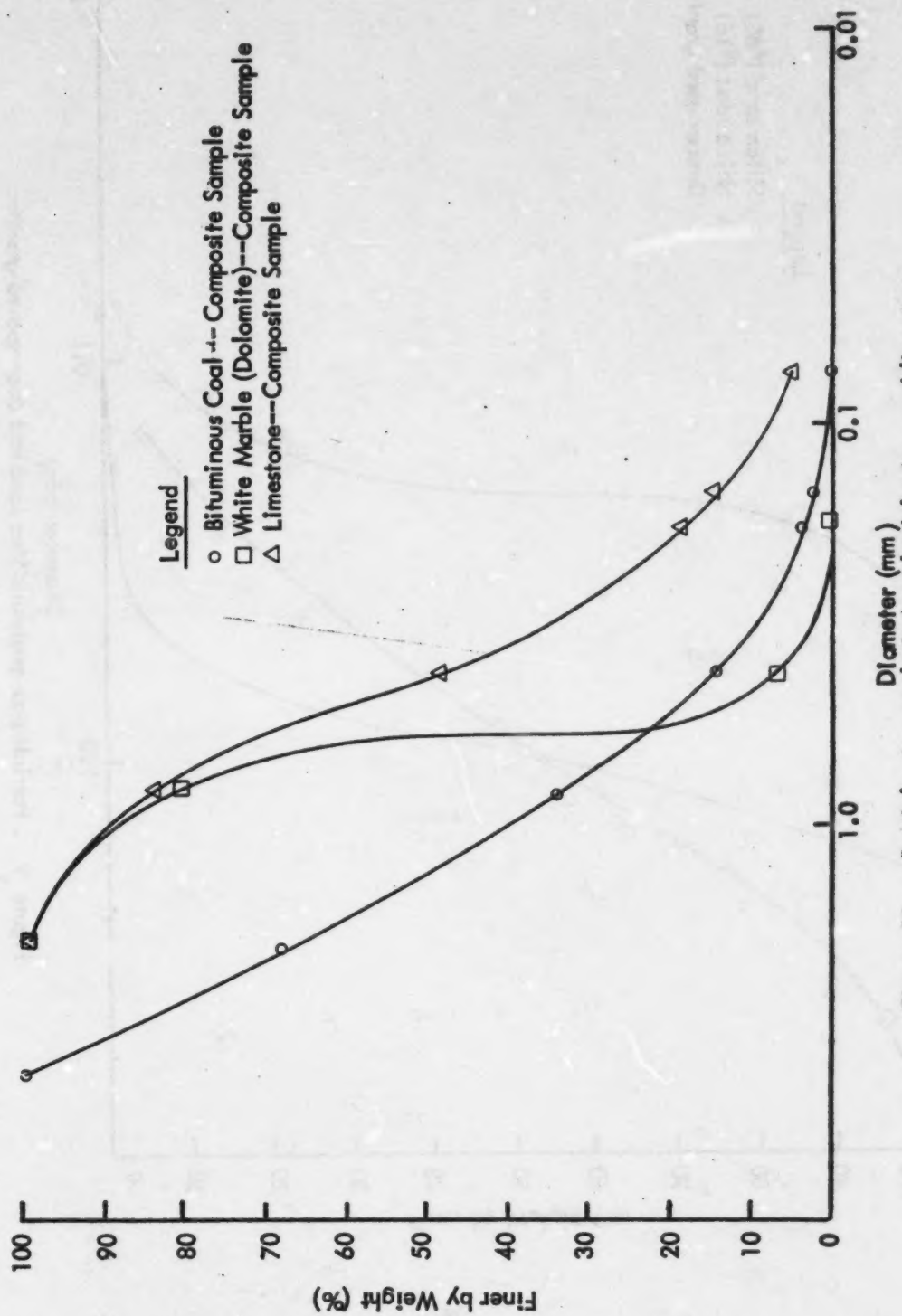


Figure 10 . Particle size analysis; coal, dolomite, and limestone.

Water-holding Capacity

Water-holding capacity was determined for the slaked residues only. A sample of slaked and dried residue was placed in a funnel lined with filter paper, covered with water, and allowed to drain under the force of gravity. The sample was covered to prevent evaporation, and allowed to stand until there was no further water drainage for a five-minute period. Then the wet sample was weighed, dried at approximately 103° C for 24 hours, and reweighed. The difference between the wet and dry weights was equal to the water held in the sample. This was divided by the dry weight of the sample to give the water-holding capacity of the residue. Results of the water-holding capacity tests are presented in Table 15.

Permeability

Data was obtained following the procedure described in the Standard Method of Test for Permeability of Granular Soils (Constant Head). The results of the tests for residue permeability are shown on Table 16.

Results

Chemical Composition

Laboratory mixing tests wherein residue was added to water to characterize their total soluble fractions are presented in Tables 17 through 20. BOD results are also shown graphically in Figure 11. Results of the laboratory bench-scale leaching tests are given in Tables 20 through 26 and Figures 12 through 14.

The procedures followed in these tests do not give absolute values, but rather data for comparison of residues. The molecular states (types of compounds) of the analyzed elements were not determined. Comparison of the laboratory mixing test characterization analyses and bench-scale small column leaching tests was a basis for planning the longer-term pilot-scale tests (Chapter 6) which simulated field conditions more closely. The laboratory tests indicated that major leachate constituents of the residues were high in total dissolved salts consisting of sulfate and chloride anions, and calcium, magnesium, iron, sodium, and potassium cations. Many trace metals were also present in low concentration, which would nevertheless be high enough to cause concern if they were leached into the environment.

Comparison of results for soluble fractions showed that pH will undoubtedly influence the quality of the leachate. In the bench-scale experiment, some elements (chloride, sodium, potassium) were leached readily, and were almost completely extracted by the time tap water equivalent to six times the weight of the residues had leached through. On the other hand, calcium and sulfate were leached in relatively constant, high concentrations which had not diminished by the end of six water addition cycles.

Sulfate content in leachate exceeded the recommended maximum for drinking water supply. Sulfate is also of interest as it may combine with calcium to form gypsum or with lead as lead sulfate. Both of these compounds are relatively insoluble, and so leaching of calcium and lead may be reduced.

TABLE 15. RESIDUE PHYSICAL PROPERTIES

Residue Type	Specific Gravity ^a (g/cc)	Moisture Content ^b (% dry wt.)	Degree of Saturation ^b (% dry wt.)	Dry Density		Water-holding Capacity $\left(\frac{\text{g H}_2\text{O}}{\text{g Residue}} \right)$
				Before Slaking ^b (g/cc)	After Slaking (g/cc)	
VFA	2.65	0	0	0.76	0.76	0.66
VSBM	c	0	0	0.92	0.97	0.50
NJFA	2.71	0	0	0.74	0.65	0.74
NJSBM	c	0	0	0.73	1.08	0.44
EFA	2.02	0	0	1.46	0.88	0.70
ESBM	c	0	0	1.36	0.67	0.98
CFA	2.72	0	0	1.09	0.78	0.76
FSFA	3.11	0	0	1.18	0.76	0.78

^a After slaking.^b As received.^c Not obtainable, as some portion of the material in question enters into solution.

TABLE 16 . PERMEABILITY OF RESIDUES AND COLUMN MATERIALS

Description	Hydraulic Conductivity K (cm/sec)
Residue	
PER Virginia fly ash	1.9×10^{-3}
PER Virginia spent bed material (slaked)	1.9×10^{-3}
Exxon New Jersey fly ash	6.4×10^{-4}
Exxon New Jersey spent bed material (slaked)	3.7×10^{-2}
Esso, England fly ash (slaked)	1.6×10^{-3}
Esso, England spent bed material (slaked)	6.8×10^{-4}
Column Material	
Limestone (granular)	1.0×10^{-2}
Dolomite (granular)	5.9×10^{-2}
Bituminous Coal (granular)	6.1×10^{-2}
Sanitary landfill	7.0×10^{-2}
Claystone (4:1, #60 sand to clay)*	1.64×10^{-3}
Sandstone (#60 sand)	3.2×10^{-2}
Sandstone (#16 sand)	7.4×10^{-2}
Clayey loam (3:1 #60 sand to soil)*	1.1×10^{-3}
Silty loam (3:1 #60 sand to soil) *	1.0×10^{-2}
Sandy loam	1.6×10^{-4}
Granite bedrock (3:1 p-gravel to decomposed granite)*	5.2×10^{-3}
Gravel	8.2×10^{-2}

* By weight

TABLE 17. LABORATORY CHARACTERIZATION OF RESIDUES^a
1. EXXON MINIPLANT, LINDEN, NEW JERSEY

Constituent	Fly Ash			Spent Bed Material		
	Water Soluble	Acid ^b Soluble	Base ^c Soluble	Water Soluble	Acid ^b Soluble	Base ^c Soluble
pH	9.3	<1.0	13.0	12.2	6.6	13.0
Total dissolved solids	2,124	-- ^e	--	4,188	--	--
COD	45.6	--	--	51.4	--	--
BOD	-- ^f	--	--	-- ^f	--	--
Chloride	ND ^d	ND	5.76	ND	ND	8.42
Nitrate	27	--	3	26	--	ND
Phosphate	4	182	6.3	ND	1.5	ND
Sulfate	1,190	5,300	26,000	1,900	1,000	17,400
Aluminum	--	--	--	0.06	0.26	ND
Arsenic	ND	62.5	22.5	5.0	30.0	18.7
Beryllium	--	--	--	ND	ND	ND
Boron	0.61	ND	0.88	0.64	ND	0.97
Cadmium	ND	0.2	0.2	ND	0.5	0.2
Calcium	1,805	34,600	ND	6,017	96,754	ND
Chromium	--	--	--	--	--	--
Copper	--	--	--	0.5	1.07	0.12
Iron	ND	78.4	1.6	ND	7.6	1.8
Lead	2.5	7.7	6.0	2.4	1.4	5.9
Magnesium	10	ND	2,360	95	ND	3,200
Manganese	--	--	--	0.025	0.95	ND
Molybdenum	ND	69	ND	12	278	ND
Nickel	--	--	--	0.5	7.7	0.75
Potassium	24	440	--	32	248	--
Silver	ND	0.2	0.4	0.02	0.6	0.3
Sodium	22	400	--	89	ND	--
Zinc	ND	8.0	0.5	ND	1.0	0.2

^a All concentrations in mg constituent/kg residue, dry weight after shaker test.

^b 1.0 N HNO₃.

^c 1.0 N NaOH.

^d None detected = ND.

^e -- Analysis not performed.

^f See Figure 11.

TABLE 18. LABORATORY CHARACTERIZATION OF RESIDUES^a
II. POPE, EVANS, & ROBBINS, ALEXANDRIA, VIRGINIA

Constituent	Fly Ash			Spent Bed Material		
	Water Soluble	Acid ^b Soluble	Base ^c Soluble	Water Soluble	Acid ^b Soluble	Base ^c Soluble
pH	12.2	4.1	12.9	12.2	6.1	12.9
Total dissolved solids	4,212	-- ^e	--	4,064	--	--
COD	104.6	--	--	57.8	--	--
BOD	--	--	--	--	--	--
Chloride	ND ^d	ND	6.21	ND	ND	22.83
Nitrate	2	--	ND	28	--	7
Phosphate	ND	2	ND	ND	ND	ND
Sulfate	1,600	1,050	17,400	1,640	1,050	32,500
Aluminum	ND	1.2	ND	0.06	0.26	ND
Arsenic	2.5	32.5	20.0	5.0	32.5	17.5
Beryllium	ND	ND	ND	ND	ND	ND
Boron	0.5	ND	0.83	0.82	ND	0.72
Cadmium	ND	0.5	0.2	ND	0.5	0.3
Calcium	540	32,000	ND	750	32,000	ND
Chromium	--	--	--	--	--	--
Copper	0.025	0.92	ND	0.5	1.07	0.12
Iron	0.5	11.0	1.7	0.1	6.6	2.2
Lead	1.6	1.3	7.1	1.1	1.5	7.6
Magnesium	96	1,940	10	22	22	ND
Manganese	0.025	0.87	ND	0.025	0.95	ND
Molybdenum	10	247	ND	11	272	7
Nickel	0.25	7.7	ND	0.5	7.7	0.75
Potassium	33	276	--	63	276	--
Silver	0.08	0.7	0.3	0.08	0.8	0.4
Sodium	145	ND	--	178	100	--
Zinc	0.08	1.1	1.0	ND	0.3	0.4

^a All concentration in mg constituent/kg residue, dry weight after shaker test.

^b 1.0 N HNO₃.

^c 1.0 N NaOH.

^d None detected = ND.

^e -- Analysis not performed.

^f See Figure 11.

TABLE 19. LABORATORY CHARACTERIZATION OF RESIDUES^a
III. ESSO, ENGLAND

Constituent	Fly Ash			Spent Bed Material		
	Water Soluble	Acid ^b Soluble	Base ^c Soluble	Water Soluble	Acid ^b Soluble	Base ^c Soluble
pH	12.2	2.4	12.9	12.1	10.8	12.9
Total dissolved solids	5,266	-- ^e	--	6,214	--	--
COD	132	116	98	68	68	59
BOD	f	--	--	f	--	--
Chloride	11,200	5,000	10,000	8,200	12,500	10,280
Nitrate	24.5	--	ND ^d	12	--	9.4
Phosphate	6.0	2.0	1.0	1.9	1.9	0.6
Sulfate	4,380	2,625	24,310	3,380	250	4,625
Aluminum	0.25	1.75	ND	0.25	1.25	1.0
Arsenic	ND	0.05	ND	ND	0.1	ND
Beryllium	ND	ND	42	ND	50	114
Boron	ND	0.325	ND	0.63	ND	0.52
Cadmium	ND	0.075	0.05	0.05	0.28	ND
Calcium	4,500	70,000	316	4,750	75,000	60
Chromium	1.75	14.2	ND	1.5	13.5	ND
Copper	ND	2.25	ND	0.5	2.0	ND
Iron	1.0	7.0	0.25	1.7	6.0	ND
Lead	0.075	ND	ND	0.17	ND	ND
Magnesium	1.0	1.3	1.0	1.0	1.3	1.0
Manganese	0.075	0.75	0.025	0.1	0.6	ND
Molybdenum	81	180	ND	0.8	ND	ND
Nickel	1.25	8.0	1.5	0.25	7.5	ND
Potassium	52	232	--	ND	ND	--
Silver	0.20	0.68	0.15	0.08	0.72	ND
Sodium	245	270	--	40	45	--
Zinc	0.15	0.3	0.025	0.15	0.30	ND

^a All concentrations in mg constituent/kg residue, dry weight after shaker test.

^b 1.0 N HNO₃.

^c 1.0 N NaOH.

^d None detected = ND.

^e -- Analysis not performed.

^f See Figure 11.

TABLE 20. LABORATORY CHARACTERIZATION OF RESIDUES^a
IV. ESSO, ENGLAND

Constituent	Fly Ash ^d			Fly Ash ^e		
	Water Soluble	Acid ^b Soluble	Base ^c Soluble	Water Soluble	Acid ^b Soluble	Base ^c Soluble
pH	12.1	6.2	12.9	12.0	6.4	13.0
Total dissolved solids	3,808	-- ^g	--	4,380	--	--
COD	197.6 ^h	--	--	252.3 ^h	--	--
BOD	--	--	--	--	--	--
Chloride	199.5	210.6	354.6	160.7	77.6	388.0
Nitrate	11.8	--	ND ^f	10.6	--	2.6
Phosphate	1.87	--	--	0.35	--	--
Sulfate	1,280	2,000	11,300	1,680	2,190	3,260
Aluminum	0.25	1.75	ND	--	--	--
Arsenic	0.1	3.7	0.3	0.1	3.4	ND
Beryllium	ND	ND	42	--	--	--
Boron	ND	ND	0.13	0.43	ND	0.07
Cadmium	ND	0.18	0.01	0.01	0.18	ND
Calcium	510	32,000	ND	520	32,000	ND
Chromium	--	--	--	--	--	--
Copper	ND	2.25	ND	--	--	--
Iron	0.46	5.23	0.25	0.43	4.78	ND
Lead	0.5	5.2	0.7	0.6	5.3	0.1
Magnesium	7	16	ND	5	13	ND
Manganese	0.075	0.75	0.025	--	--	--
Molybdenum	17	229	ND	12	2.7	ND
Nickel	1.25	8	1.5	--	--	--
Potassium	56	356	--	62	276	--
Silver	0.04	0.53	ND ^f	0.03	0.50	ND
Sodium	300	800	--	200	200	--
Zinc	0.03	0.13	ND	ND	0.10	ND

^a All concentrations in mg constituent/kg residue, dry weight after shaker test.

^b 1.0 N HNO₃.

^c 1.0 N NaOH.

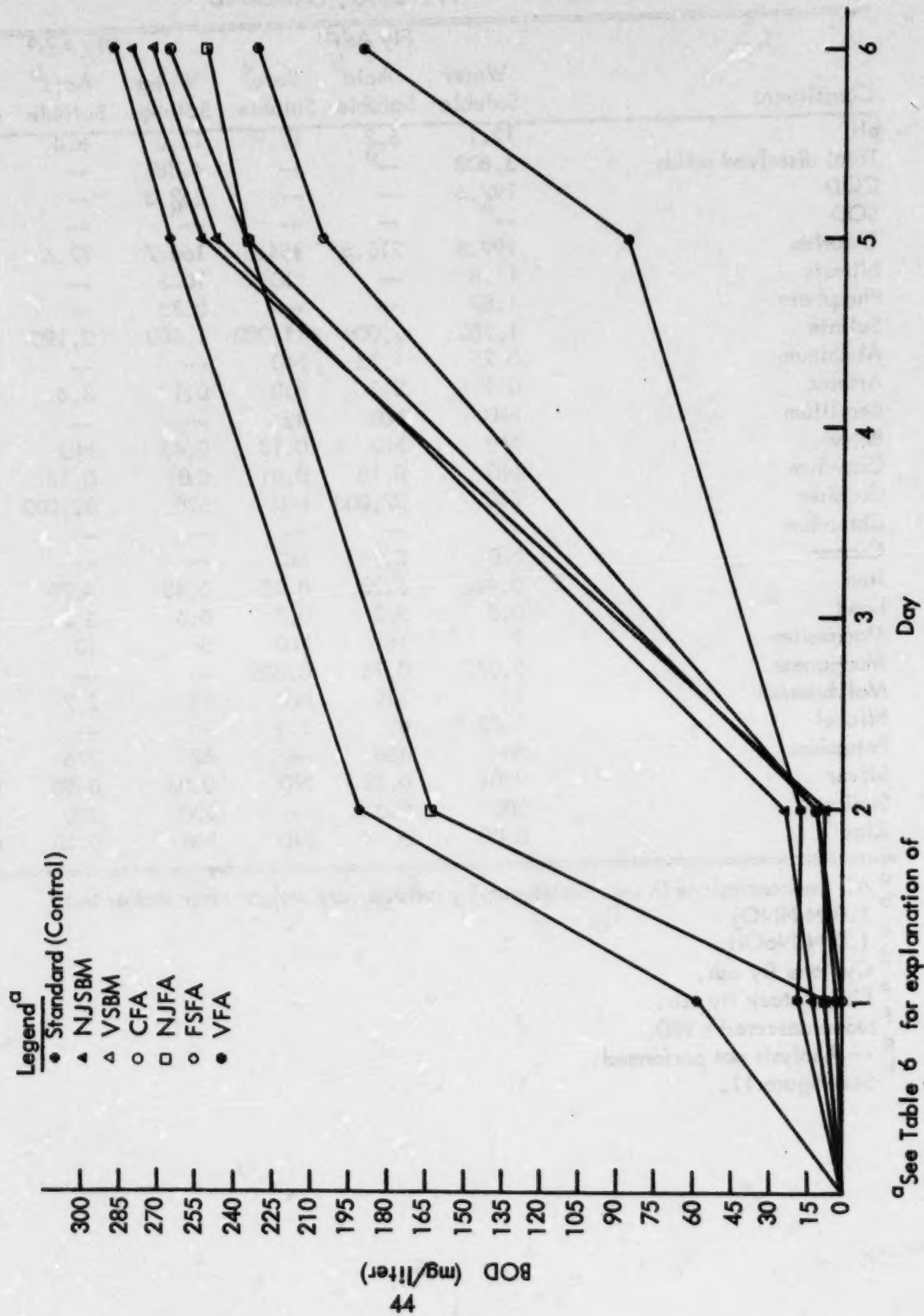
^d Cyclone fly ash.

^e Fines, stack fly ash.

^f None detected = ND.

^g -- Analysis not performed.

^h See Figure 11.



^aSee Table 6 for explanation of letter code.

Figure 11 . BOD from residue water extract¹.

TABLE 21. LABORATORY LEACHING^b TESTS: GRANITE BEDROCK

Constituent ^c	Total Volume of Leachate (ml)		
	250	500	750
pH	9.2	8.8	8.9
Chloride	ND ^a	ND	ND
Nitrate	ND	ND	--
Sulfate	34.0	10.0	2.5
Arsenic	2.5	ND	0.8
Boron	--	--	ND
Cadmium	ND	--	ND
Calcium	1.0	ND	ND
Iron	ND	ND	ND
Lead	ND	ND	ND
Magnesium	ND	ND	ND
Mercury	--	ND	ND
Potassium	ND	ND	ND
Sodium	72.0	60.0	64.0
Zinc	ND	ND	ND

^a ND - None detected.

^b Water percolated through the bench scale residue sample.

^c Mg/l except as noted.

TABLE 22. LABORATORY LEACHING TESTS^b: BITUMINOUS COAL

Constituent ^c	Total Volume of Leachate (ml)		
	250	500	750
pH	9.0	8.8	8.8
Chloride	ND ^a	ND	ND
Nitrate	ND	ND	--
Sulfate	232.0	42.0	10.0
Arsenic	2.5	5.0	2.5
Boron	--	--	ND
Cadmium	ND	--	ND
Calcium	3.6	0.3	0.9
Iron	ND	ND	ND
Lead	ND	ND	ND
Magnesium	ND	ND	ND
Mercury	ND	ND	ND
Potassium	4.0	ND	1.0
Sodium	80.0	56.0	64.0
Zinc	ND	ND	ND

^a ND - None detected.

^b Water percolated through the bench scale residue sample.

^c Mg/l except as noted.

TABLE 23. LABORATORY LEACHING^b TESTS: DOLOMITE

Constituent ^c	Total Volume of Leachate (ml)		
	250	500	750
pH	9.6	8.8	9.2
Chloride	ND ^a	ND	ND
Nitrate	ND	ND	ND
Sulfate	9.0	3.0	ND
Arsenic	0.8	0.8	0.8
Boron	--	--	0.6
Cadmium	ND	--	ND
Calcium	2.2	0.1	ND
Iron	ND	ND	ND
Lead	0.1	ND	ND
Magnesium	ND	ND	ND
Mercury	ND	ND	ND
Potassium	8.0	ND	ND
Sodium	103.0	61.0	60.0
Zinc	ND	ND	ND

^a ND - None detected.

^b Water percolated through the bench scale residue sample.

^c Mg/l except as noted.

TABLE 24. LABORATORY LEACHING^b TESTS: LIMESTONE

Constituent ^c	Total Volume of Leachate (ml)		
	250	500	750
pH	9.5	8.8	8.9
Chloride	ND ^a	ND	ND
Nitrate	ND	ND	--
Sulfate	10.0	19.0	6.0
Arsenic	ND	1.6	1.6
Boron	--	--	0.7
Cadmium	0.01	--	0.01
Calcium	ND	ND	ND
Iron	ND	ND	ND
Lead	0.6	ND	ND
Magnesium	ND	ND	ND
Mercury	ND	ND	ND
Potassium	3.0	ND	1.0
Sodium	74.0	68.0	63.0
Zinc	ND	ND	ND

^a ND - None detected.

^b Water percolated through the bench scale residue sample.

^c Mg/l except as noted.

TABLE 25. LABORATORY LEACHING^b TESTS: #60 SILICA SAND

Constituent ^c	Total Volume of Leachate (ml)		
	250	500	750
pH	9.0	8.8	9.1
Chloride	75.0	ND ^a	ND
Nitrate	ND	ND	--
Sulfate	123.0	30.0	5.0
Arsenic	ND	ND	1.6
Boron	--	--	ND
Cadmium	0.01	--	ND
Calcium	ND	ND	ND
Iron	ND	ND	ND
Lead	ND	ND	ND
Magnesium	ND	ND	0.7
Mercury	ND	ND	ND
Potassium	3.0	ND	2.0
Sodium	168.0	77.0	70.0
Zinc	ND	ND	ND

^a ND - None detected.

^b Water percolated through the bench scale residue sample.

^c Mg/l except as noted.

TABLE 26. LABORATORY LEACHING^E TESTS: #16 SILICA SAND

Constituent ^C	Total Volume of Leachate (ml)		
	250	500	750
pH	10.0	8.8	8.8
Chloride	9.0	ND ^a	ND
Nitrate	ND	ND	--
Sulfate	103.0	12.0	7.0
Arsenic	0.8	ND	ND
Boron	--	--	0.025
Cadmium	ND	--	ND
Calcium	3.7	ND	ND
Iron	ND	ND	ND
Lead	0.2	ND	ND
Magnesium	ND	0.03	ND
Mercury	ND	ND	ND
Potassium	50.0	ND	ND
Sodium	245.0	68.0	62.0
Zinc	ND	ND	ND

^a ND - None detected.

^b Water percolated through the bench scale residue sample.

^c Mg/l except as noted.

TABLE 27. LABORATORY LEACHING^b TESTS: CLAYSTONE

Constituent ^c	Total Volume of Leachate (ml)		
	250	500	750
pH	9.2	8.8	9.0
Chloride	65	ND ^a	ND
Nitrate	ND	ND	--
Sulfate	141.0	9.0	2.5
Arsenic	0.8	1.6	1.6
Boron	--	ND	ND
Cadmium	ND	--	ND
Calcium	0.4	ND	ND
Iron	0.1	ND	ND
Lead	ND	ND	ND
Magnesium	0.1	ND	ND
Mercury	ND	ND	ND
Potassium	ND	ND	ND
Sodium	161.0	97.0	71.0
Zinc	ND	ND	ND

^aND - None detected.

^bWater percolated through the bench scale residue sample.

^cMg/l except as noted.

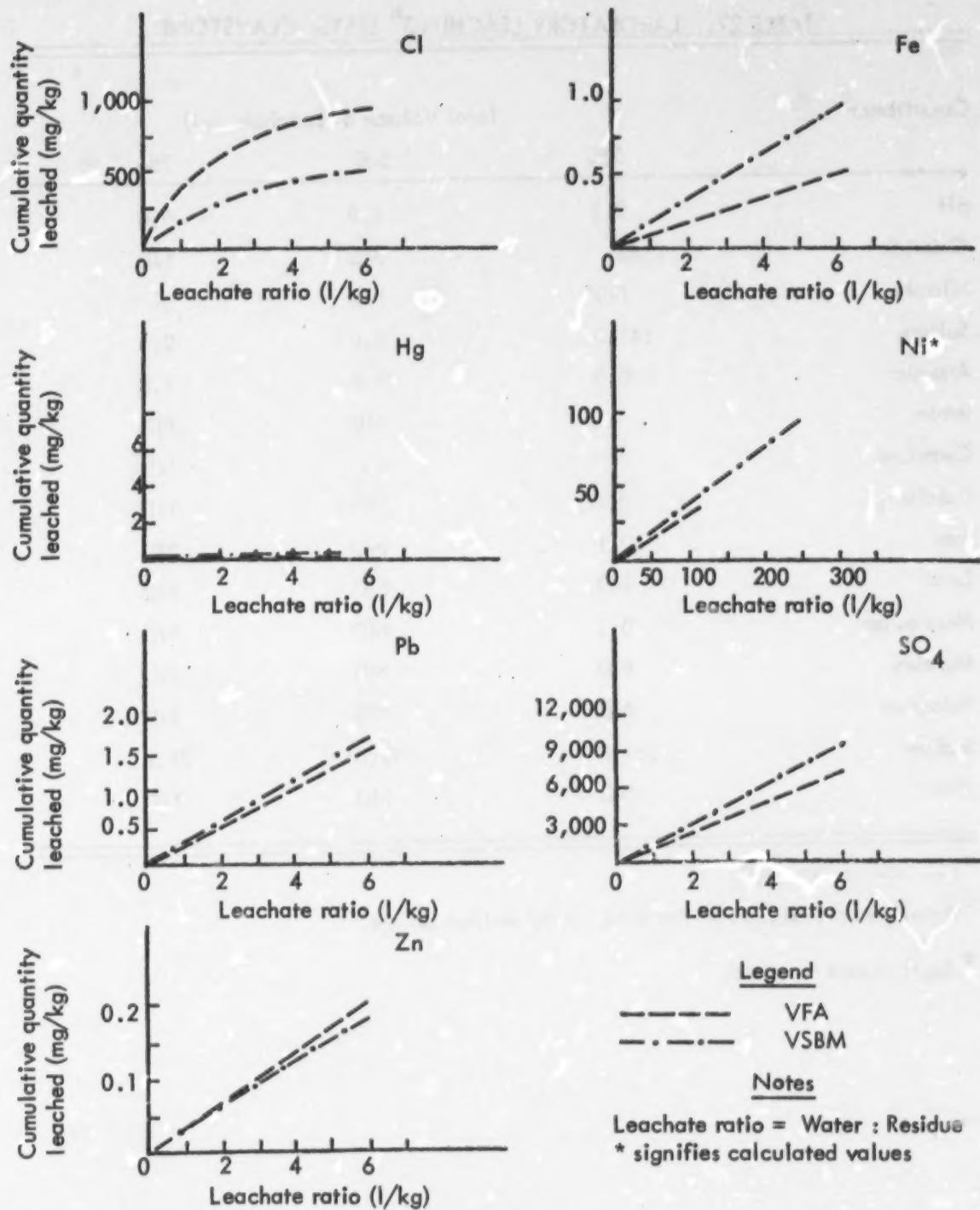


Figure 12. Leaching characteristics of VFA and VSBM.

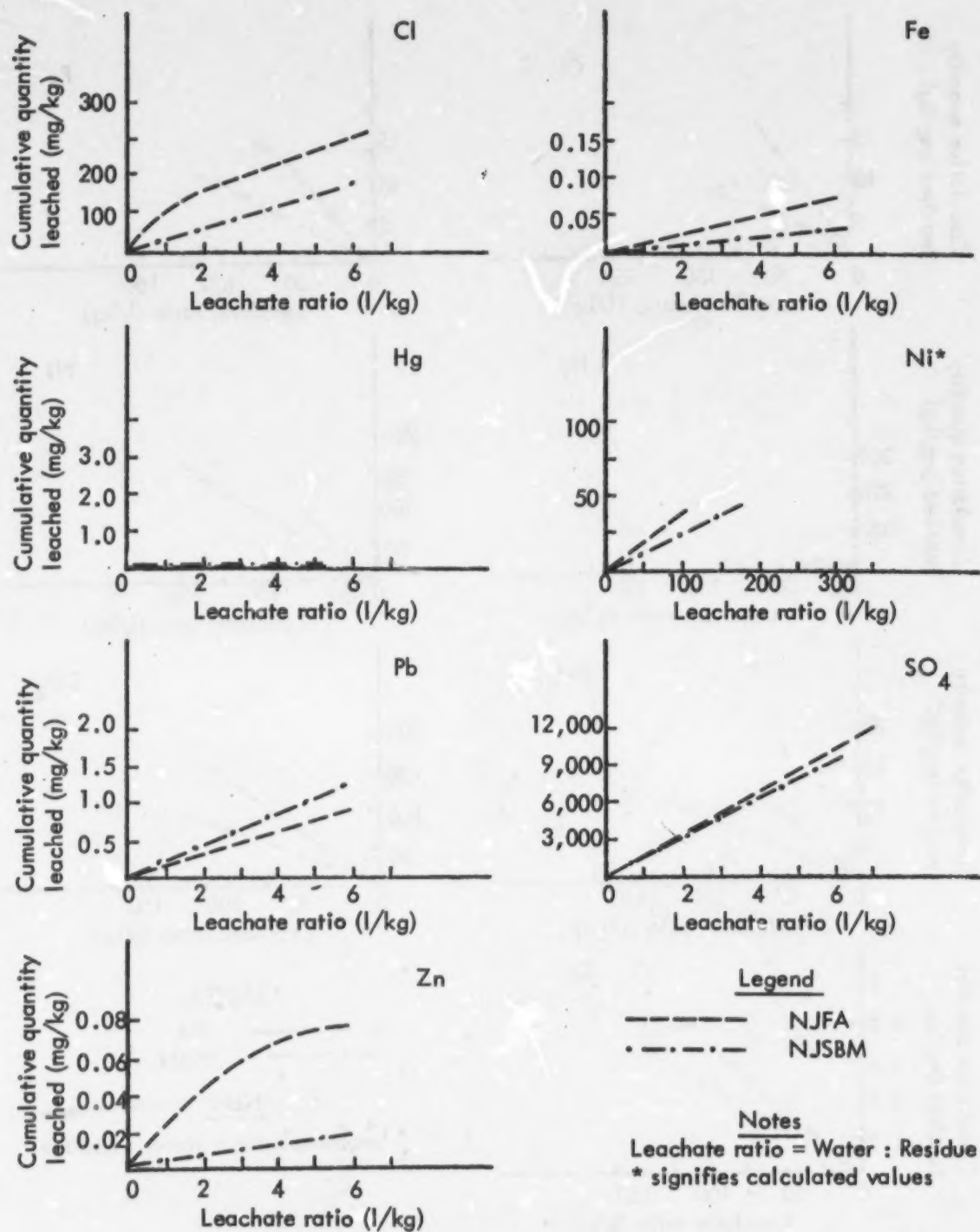


Figure 13 . Leaching characteristics of NJFA and NJSBM.

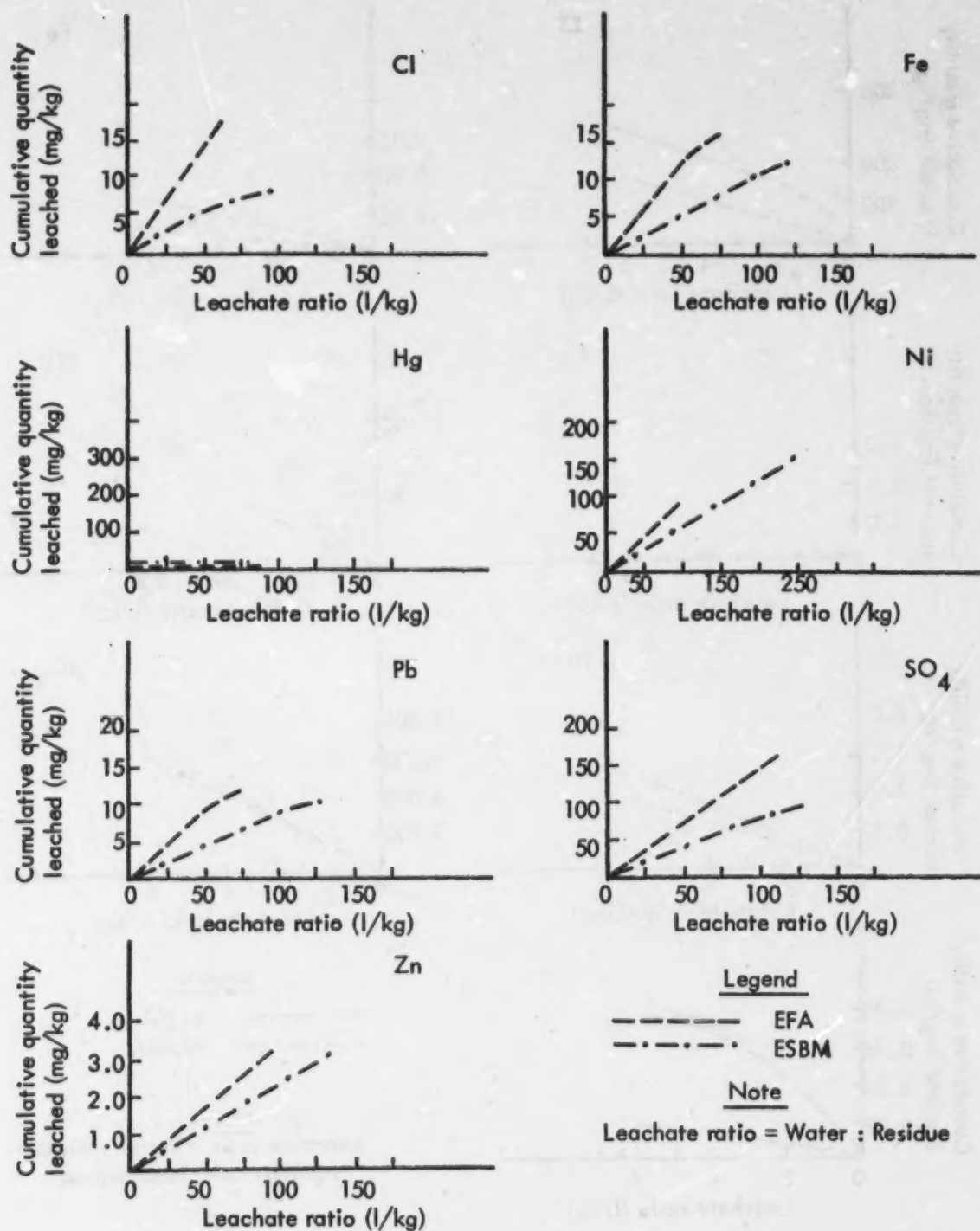


Figure 14. Leaching characteristics of EFA and ESBM.

CHAPTER 6

PILOT COLUMN STUDIES OF RESIDUE DISPOSAL

Purpose

One purpose of this study was to evaluate the possible impacts of residue disposal into different locations. The first step in this evaluation was to simulate likely disposal locations on a pilot scale. This allowed testing under defined conditions and control of physical variables which might affect the behavior of the residues in natural environments. The following section discusses the real world and simulated disposal locations that were evaluated.

Simulated Sedimentary Environment Columns

Ocean Disposal

Actual location. Residue wastes could be disposed into the ocean in many ways which include dumping the wastes into the open ocean, piping the wastes in the form of a slurry onto the ocean floor (or a submarine canyon), or using the residues to build land or islands.

Test Column. The ocean disposal test column is more representative of a filled land type disposal in the ocean where only the tidal portion of the residue would be flushed by sea water for an extended period of time (also waves and land drainage can cause some flushing). The #60 sand used in the test column represents the deposited sandy base over which the residues might be placed when filling begins (see Figure 15; for legend see Figure 16).

Sanitary Landfills

Actual Location. Sanitary landfills are made of materials (a mix of ash residues and solid waste) and lifts of soil placed on natural ground or other inert material. Sanitary landfills may be built with 3m of mixed refuse to 0.3m of soil fill/lift), i.e.

~ 90 percent solid waste and ~ 10 percent cover soil. The residue to trash percentage combination may vary. Both residues and refuse landfills can generate leachate when saturated with water.

Test Column. The test column simulated an arbitrarily selected real world landfill environment where a brown municipal type solid waste mixture was placed on a sequence of sedimentary strata overlying granite bedrock (see Figure 18). Organic solid waste and ash residues were separated for residue reclamation after leaching tests. Assuming a depth of 30m below the land surface for the water table, each column represented the conversion factors for the thicknesses of the replicated real world strata materials as shown in Table 28. The scale coefficients of approximately 1:12 were chosen to conveniently replicate the strata in the test column assuming a 30.5 m depth to groundwater. Relatively impermeable

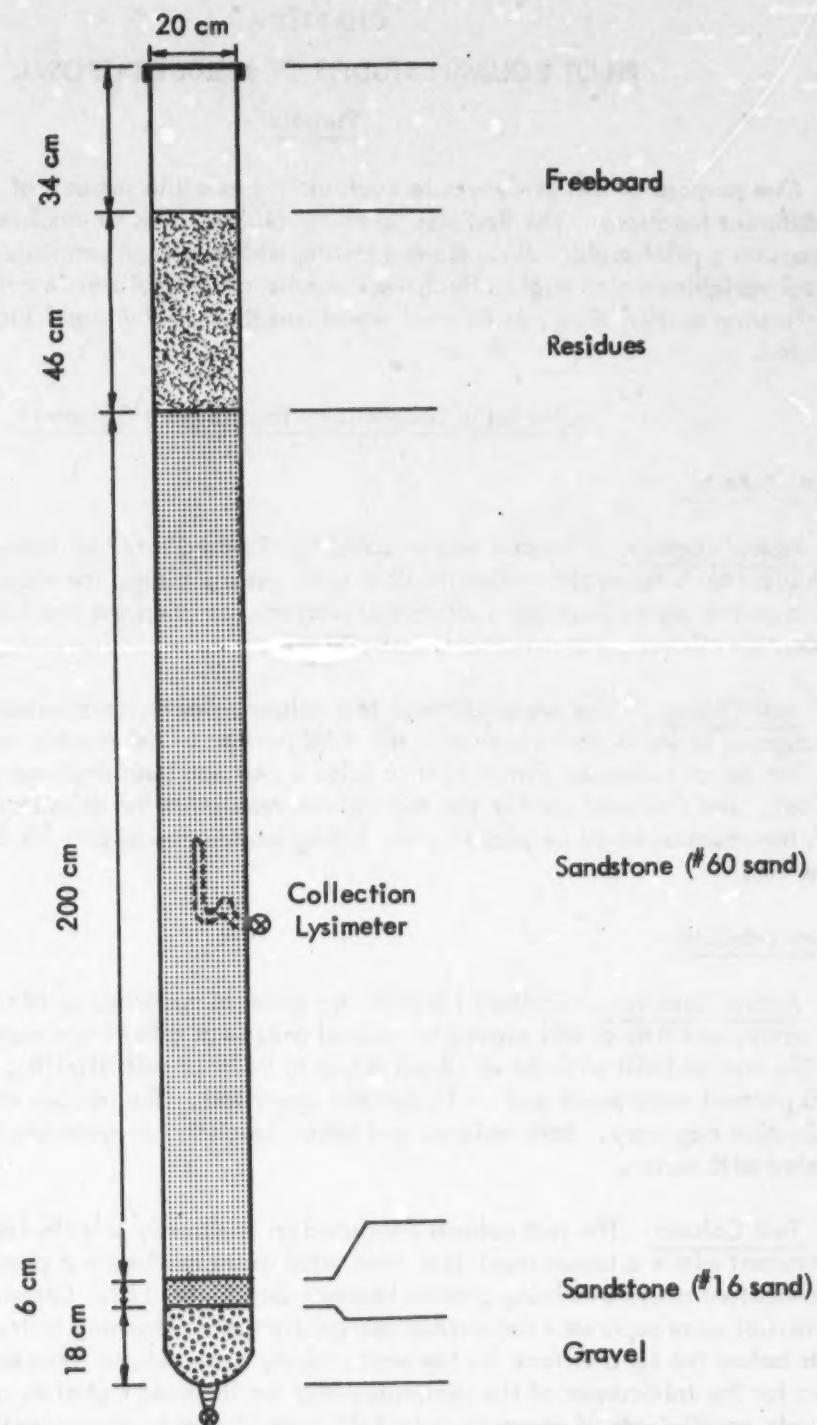


Figure 15. Simulated sedimentary environment: sea water test column.

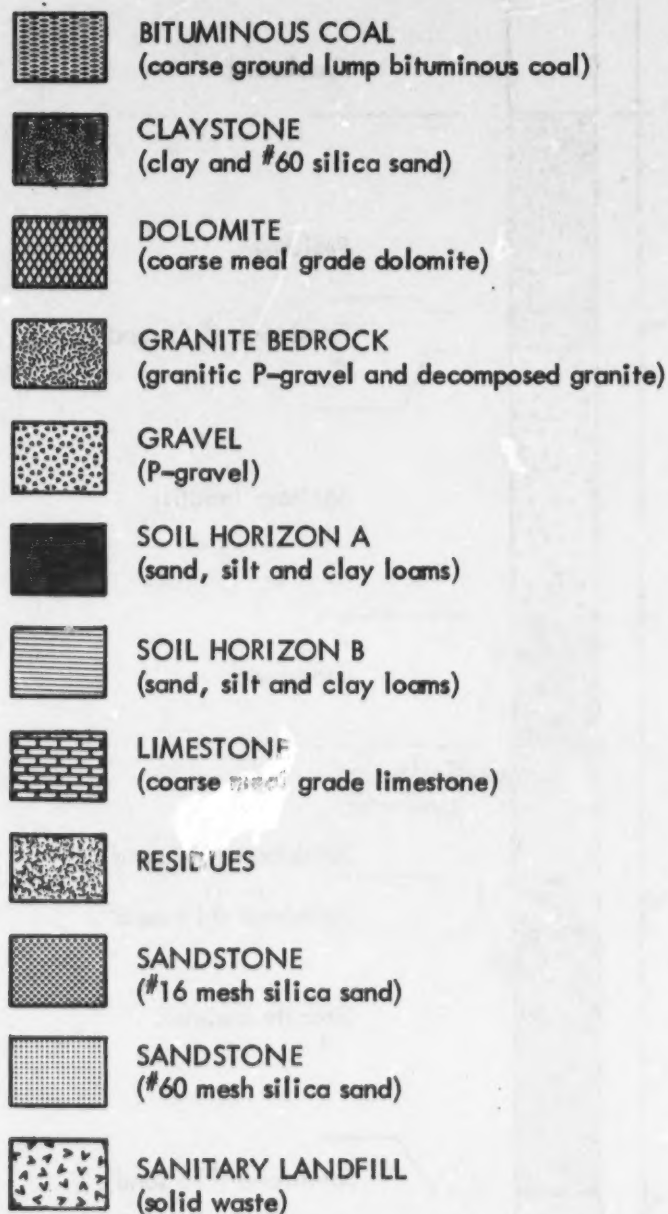


Figure 16 . Legend for test column disposal environments.

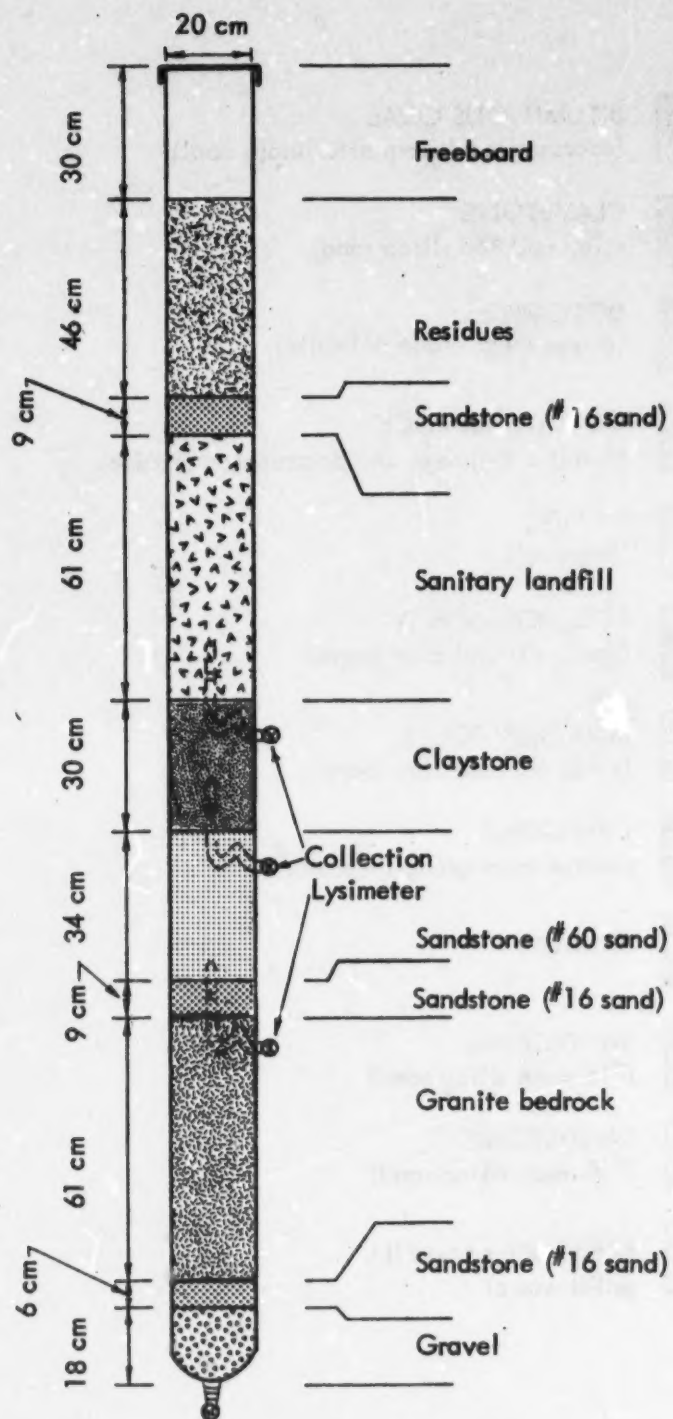


Figure 17. Sanitary landfill test column.

TABLE 28. REPRESENTATIVE THICKNESS SANITARY LANDFILL
SIMULATED IN TEST COLUMNS

Material	Representative Stratum Thickness (m)	Column Layer Thickness (m)	Scale Coefficient ^d
Residue	5.79	0.46	1:12.6
Solid Waste ^a	7.62	0.61	1:12.5
Claystone ^b	0.91	0.29	1: 3.1
Sandstone ^c	8.54	0.67	1:12.8
Granite Bedrock	7.62	0.61	1:12.5

^a No decomposition before leaching began in first 20 columns, "fresh" solid waste used.

^b Excludes admixed #60 sand.

^c Includes admixed #60 sand from claystone layer.

^d Thickness of strata in field to thickness of simulated strata in test column (a ratio).

Source: Ralph Stone and Company, Inc. files.

materials, such as claystone, were "diluted" with sand to increase their permeability, thus resulting in reduced scale coefficients. Obviously, standard claystone is so impervious that without the increase in permeability provided by the standard Ottawa sand, there would have been no significant column leachate. In nature, however, there is slow water movement and leaching through the claystone. Hence, the test columns replicated an accelerated-type leachate test of what could occur in nature.

Limestone and Dolomite Quarries

Actual Location. An abandoned limestone quarry might contain 20 to 40 percent limestone; the remaining unquarried limestone could normally be left because it was of poor quality, had a high cost of mining, or for other reasons. The sedimentary sequence which would be associated with the quarry would probably consist of a series of limestone, shale, and sandstone beds. This type of strata occurs in varying percentages relative to each other. No "typical" section below a limestone or dolomite quarry exists. It might be all sandstone, all shale, or a combination of any of the three types of strata. For this reason, an arbitrary "typical" sequence was selected from a real world quarry as shown in Table 29.

Test Column. The test columns represent a configuration in which residues would be deposited in an abandoned quarry pit and underlain by the thickness of strata shown in Table 28 (assuming a depth to groundwater table of 30 m). In this 30 m section, below the residues there would be 14.2 m of limestone, 1.6 m of claystone, and 14.2 m of sandstone. (See Figures 18 and 19.) Again, claystone was admixed with sand to increase permeability, thus, resulting in lower scale coefficients.

Coal Mine.

Actual Location. An abandoned coal mine would be underlain by a sequence of shale, sandstone, limestone, and minor coal seams - the sequence being predominantly shale (see Figure 20). Disposal of residues would be in an abandoned mine underlain by similar strata.

Test Column. The test column represents an abandoned coal mine which is underlain by the thicknesses of strata, as shown in Table 30 and Figure 21 (assuming a 30 m depth to groundwater).

Ratios of Densities

Ratios of densities shown in Table 31 are calculated by comparing the densities of materials as they exist in the columns with densities of materials as they could exist in the field. The densities of materials in the test columns were calculated using the actual weights of materials added, divided by the amount (height) of column filled up (see Table 32). Densities of typical earth materials in the field were determined from various sources (see Table 33). Comparison of Tables 31 and 32 indicate that the actual densities of materials placed in the columns were less than may exist under field conditions.

TABLE 29. REPRESENTATIVE THICKNESSES OF LIMESTONE &
DOLOMITE SIMULATION TEST COLUMNS

Limestone Quarry			Dolomite Quarry		
Material	Representative Stratum Thicknesses (m)	Scale (a) Coefficient	Material	Representative Stratum Thicknesses (m)	Scale (a) Coefficient
Limestone	14.2	15.7	Dolomite	14.2	15.7
Claystone ^b	1.4	3.9 ^c	Claystone	1.4	3.9 ^c
Sandstone ^d	14.2	15.7	Sandstone	14.2	15.7

^a Thickness of layer in field to thickness of simulated layer in column.

^b Excludes add-mixed #60 sand.

^c As mixed, includes sand with clay in column, for increased permeability.

^d Includes add-mixed #60 sand from claystone layer.

* Source: 30, 49, 106.

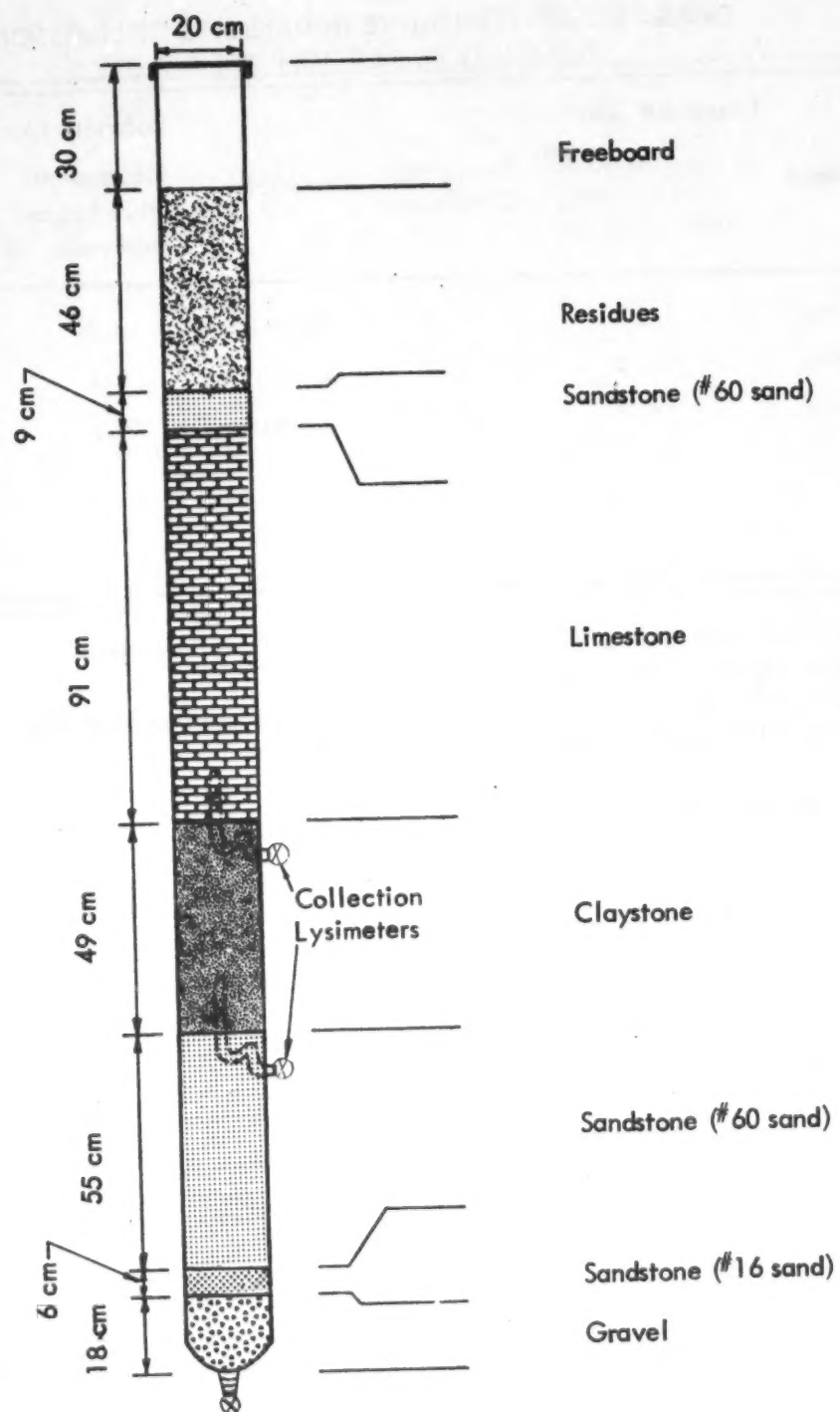


Figure 18 . Abandoned limestone quarry test column.

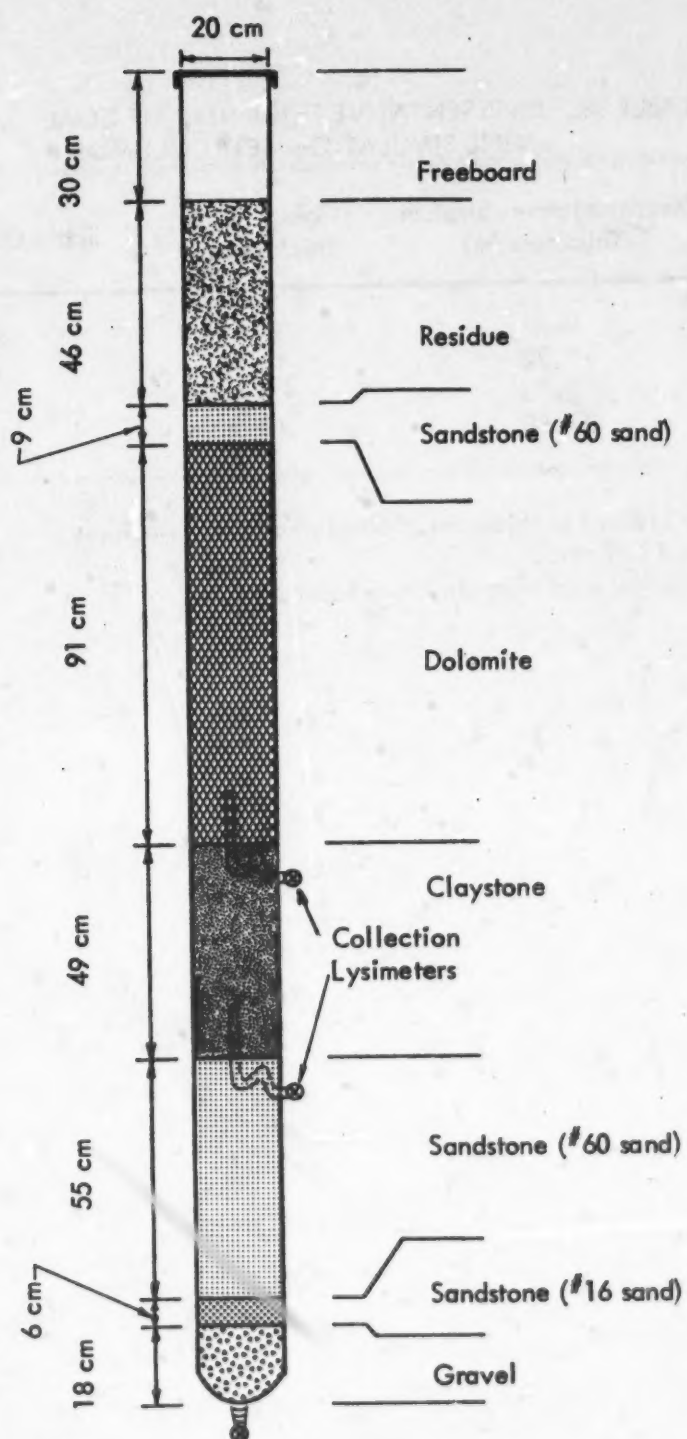


Figure 19. Simulated sedimentary environment: dolomite quarry test column.

TABLE 30. REPRESENTATIVE THICKNESS OF COAL
MINE SIMULATION TEST COLUMNS

Material	Representative Stratum Thickness (m)	Column Layer Thickness (m)	Scale Coefficient ^a
Bituminous Coal	9.45	0.611	15.5
Limestone ^b	7.32	10.46	15.8
Claystone ^c	2.13	0.551	3.9
Sandstone ^c	11.58	10.73	15.8

^a Thickness of layer in field to thickness of simulated layer in column.

^b Excludes add-mixed #60 sand.

^c Includes add-mixed #60 sand from claystone layer.

Source: 106.

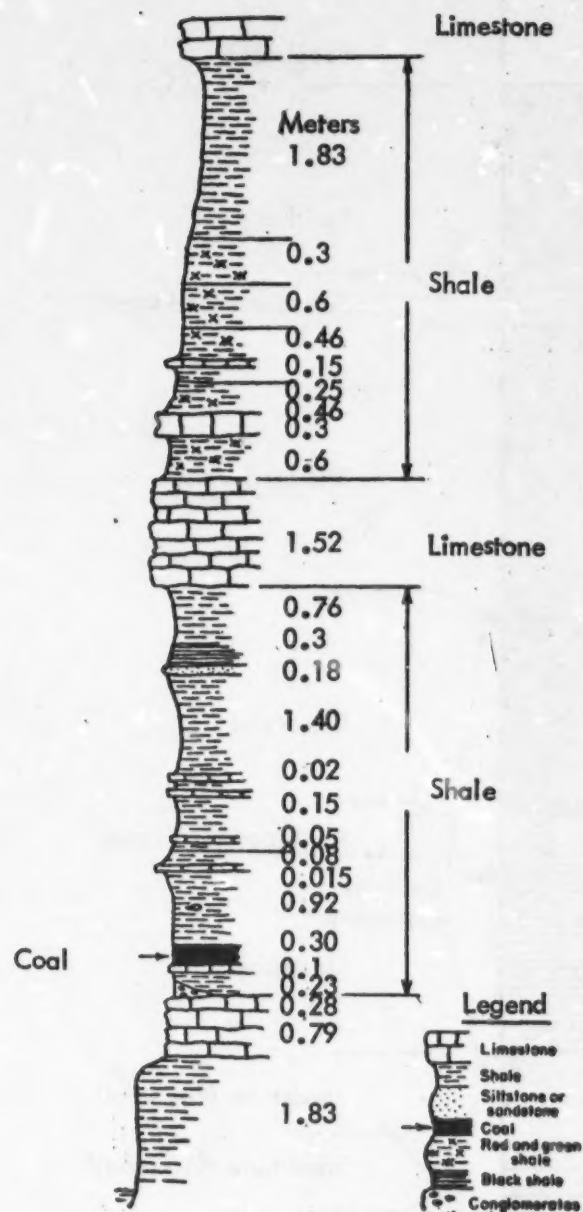


Figure 20: Stratigraphic section of a typical coal mine.

Source: 106.

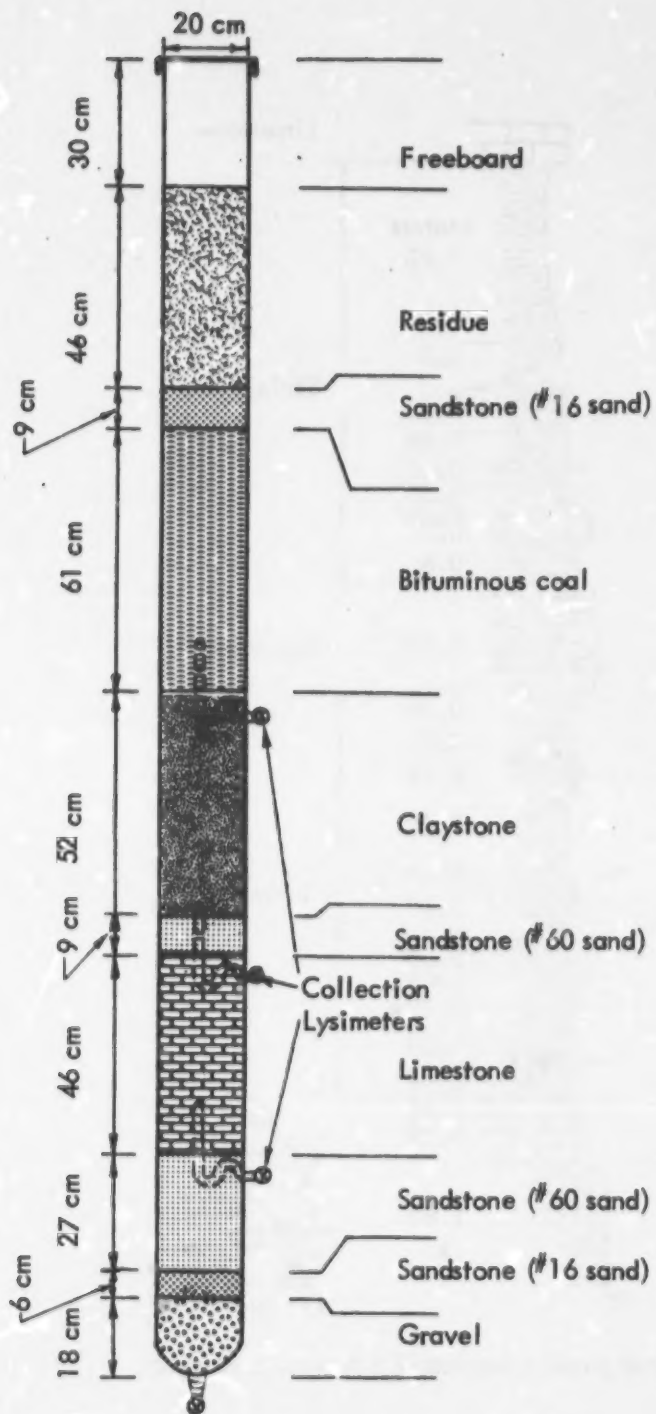


Figure 21. Abandoned coal mine test column.

TABLE 31. MATERIAL DENSITIES OF FIELD STRATA AND TEST COLUMNS

Material in Column	Density (g/cc)	Material in Field	Density (g/cc)	Ratio of Densities	
				Column: Field	Field: Column
Limestone	1.76	Limestone	2.71	1.54:1	1:0.65
Dolomite	1.51	Dolomite	2.85	1.89:1	1:0.53
P-Gravel	2.16	Granodiorite	2.72	1.26:1	1:0.79
#16 Silica	1.56	Sandstone	2.32	1.49:1	1:0.67
#60 Silica	1.56	Sandstone	2.32	1.49:1	1:0.67
Claystone	1.44 ^a	Shale	2.42	1.68:1	1:0.60
Granite Bedrock	1.82	Granodiorite	2.72	1.49:1	1:0.67
Solid Waste	0.63	Sanitary Landfill	0.594	1.06:1	1:0.94
Bituminous Coal	0.89	Bituminous Coal	1.25	0.71:1	1:1.40

^a Includes admixed #60 sand.

TABLE 32. MATERIAL DENSITIES OF NATURAL STRATA AND TEST COLUMNS

Material	Wt. Added (Kg)	Height (cm)	Test Column		Density (g/cc)	Density of Field Rocks (g/cc)
			Area	Volume (cu cm)		
P-Gravel	12.2	18	314.16	5,654.88	2.16	N.A. ^e
#16 Silica Sand	5.4	6	314.16	1,884.96	2.86	2.32 ^a
	6.4	9	314.16	2,827.44	2.26	2.32
#60 Silica Sand	27.2	55	314.16	17,278.8	1.57	2.32
	97.7	200	314.16	62,832.0	1.55	2.32
Clay: Sand ^b	22.2	49	314.16	15,393.8	1.44	2.42 ^c
	23.6	52	314.16	16,336.3	1.44	2.42
Limestone	50.3	91	314.16	28,588.6	1.76	2.71
	25.9	46	314.16	14,451.4	1.93	2.71
Dolomite	43.1	91	314.16	28,588.6	1.51	2.85
Granite Bedrock	34.9	61	314.16	19,163.76	1.82	2.72 ^d
Solid Waste	12.2	61	314.16	19,163.76	0.63	0.594
Coal	17.2	61	314.16	19,163.8	0.89	1.25
Clay w/out Sand	5.55	12.25	314.16	3,848.5	1.44	2.42 ^c

^aSandstone^b1:3 by weight^cShale^dGranodiorite^eNot available

TABLE 33. AVERAGE FIELD DENSITIES OF MATERIALS

Material	Average Field Densities (g/cc)
Granite	2.667 ^a
Granodiorite	2.716 ^a
Sandstone	2.32 ^a
Shale	2.42 ^a
Limestone	2.71 ^b
Dolomite	2.85 ^b
Sanitary Landfill	0.594

^aSource: 51.^bSource: 98.

The materials in the test columns were prepared by granulation and hence have greater surface area exposed for chemical reactions than the natural rocks. In the field the natural rocky materials would have less surface area exposed to water percolating through the strata. The amount of surface area exposed in the field per meter of strata is a variable depending on porosity, capilarity and the extent of fractures and/or permeability for each material. No simple comparison can therefore be made of surface area exposed per meter of column material versus the surface area exposed per meter of stratum in the field.

Column Test Procedures

Column Construction

The test columns were made from plastic PVC pipe (20.3 cm ID) cut to 3.05 m lengths. For each simulated disposal environment, stratigraphic configurations were developed during the literature search and scaled to fit the columns. Table 34 identifies the columns constructed by number code, environment, and residue type tested. The simulated environment was marked on the column, as were locations for layer interfaces, observation ports and soil moisture (lysimeter) ports. The lysimeter and observation ports (2.54 cm diameter) were drilled in the column sides. A 1.59-cm port was drilled in the center of the PVC bottom cap for each column and a plastic drain spout was glued in place. The columns were washed clean, dried, and the bottom cap was glued to the pipe; finally, the columns were bracketed to the wall in a vertical position.

Filter paper (20.3 cm diameter, #1 qualitative) with a plastic screen above (20.3 cm diameter) was placed in the bottom of the column. These items were installed from the top and their location adjusted with a long pole to obtain their correct position. The columns were then ready for partial filling.

Lysimeter Assembly

A porous ceramic cup (1-bar) was attached to a 30.5 cm length of polyethylene tubing (1.27 cm ID). The ceramic cup and 3 to 5 cm of the tubing were then covered with a 0.64 cm layer of #200-mesh silica sand, applied in a thick slurry. The lysimeters used an absorbent cotton sock to hold the fine sand during and after placement in the test columns. Figure 22 illustrates the lysimeter assembly and its placement in the columns.

Column Material Preparation

Standard particle size analyses were performed on all materials added to the columns (see Figures 6 through 10). Detailed grading analyses were employed in the column design: 1) to prevent erosion and clogging (piping of finer material through coarser materials); 2) to provide sufficient permeability to allow leaching; and 3) to assure classified reproducible grain sizes and materials. Table 35 presents the criteria used, and Table 36 summarizes the results of the grading analysis.

TABLE 33. COLUMN AND RESIDUE IDENTIFICATION

Column No.	Environment	Residue	No.	Date	Operating Conditions of Test Run ^a					Average Temperature (°C)	Fuel Type	Excess Air (%)	Bed Sorbent	Ca/S mfr	Average Flue SO ₂ (ppm)
					NA ^b	VSBM	NJSBM	VSBM	NA						
1	Ocean	VSBM	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA	843	Sewickley coal	18	Germany Valley limestone	Variable	Variable
2	Limestone	NJSBM	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA	905-910	Champion coal (eastern)	9.4	Germany Valley limestone	2.5	360
3	Limestone	VSBM	NA			VSBM									
4	Limestone	NJFA	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA						
5	Limestone	VFA				VSBM									
6	Dolomite	VSBM				VSBM									
7	Dolomite	NJSBM	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA						
8	Dolomite	NJFA	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA						
9	Dolomite	VFA				VSBM									
10	Landfill	VFA	NA			VSBM				843	Sewickley coal	18	Germany Valley limestone	Variable	Variable
11	Landfill	VSBM				VSBM									
12	Landfill	NJFA	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA						
13	Landfill	NJSBM	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA						
14	Coal mine	VSBM				VSBM									
15	Coal mine	NJSBM	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA						
16	Coal mine	NJFA	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA						
17	Coal mine	VFA				VSBM									
18	Ocean	NJFA	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA						
19	Ocean	NJSBM	19.7	8-28-75	NA	VSBM	NJSBM	VSBM	NA						
20	Ocean	VFA				VSBM									

(continued)

TABLE 33 (Cont.)

Column No.	Environment	Residue	No.	Date	Operating Conditions of Test Run ^a						Ca/S mfr	Average Flue SO ₂ (ppm)
					Average Temperature (°C)	Fuel Type	Excess Air (%)	Bed Sorbent				
21	Ocean	EFA	NA	11-10-75	890	#2 oil	5-10	BCR 1359 lime	1	200		
22	Ocean	ESBM										
23	Limestone	EFA										
24	Limestone	ESBM										
25	Dolomite	EFA										
26	Dolomite	ESBM										
27	Landfill	EFA										
28	Landfill	ESBM										
29	Coal mine	EFA										
30	Coal mine	ESBM										
31	Sandy loam	EFA										
32	Sandy loam	ESBM										
33	Clay loam	EFA										
34	Clay loam	ESBM										
35	Silty loam	EFA										
36	Silty loam	ESBM										

^a Operating conditions at the pilot plant test site.^b NA - Not available.

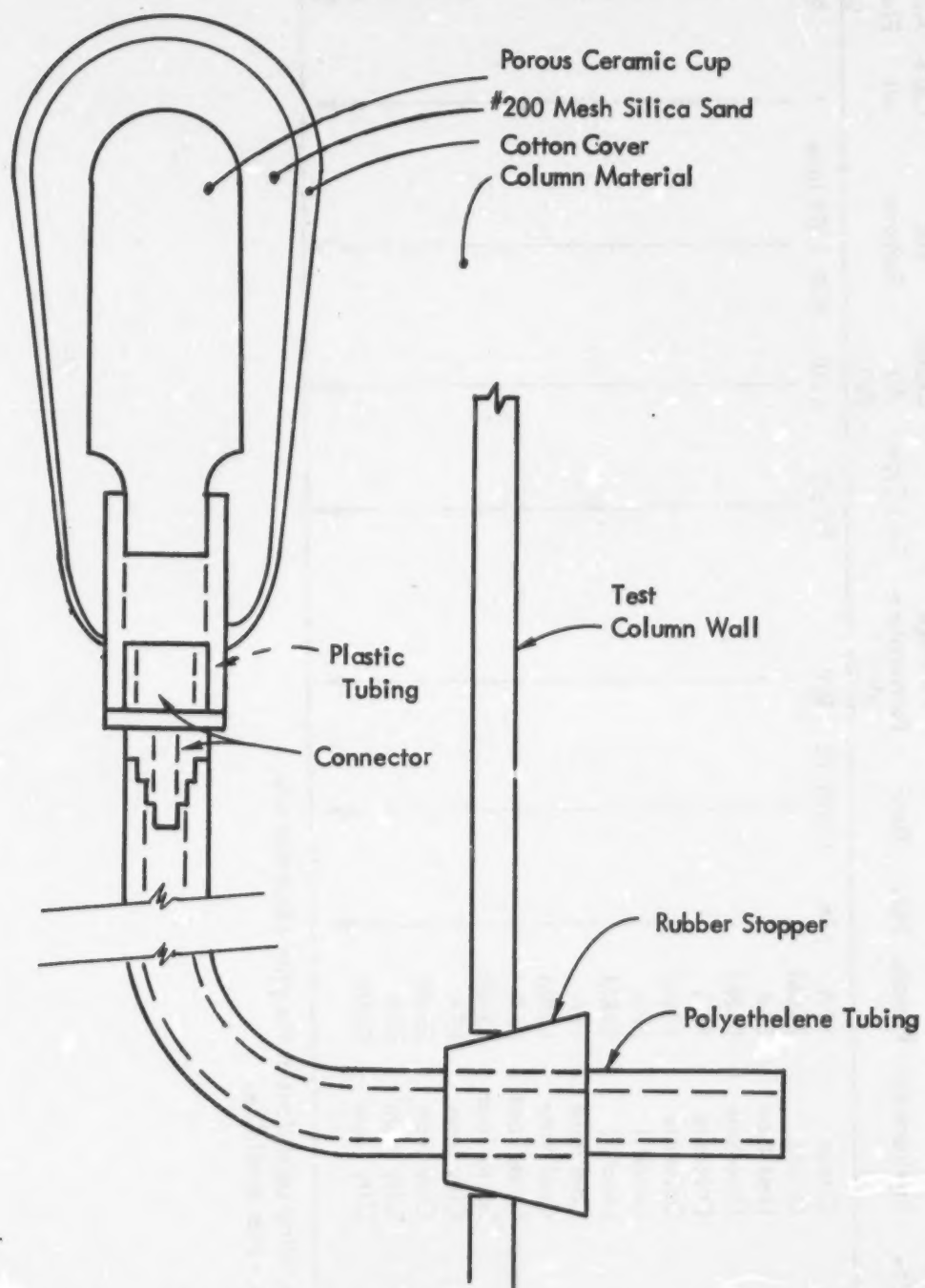


Figure 22. . Lysimeter construction and test column placement.

TABLE 35. CRITERIA DEFINITION FOR GRADING ANALYSIS

Objective	Criteria ^{a,b}
1) Prevention of erosion and clogging (piping of finer material through coarser material)	$\frac{D_{15} \text{ (filter)}}{D_{85} \text{ (soil)}} < 4 \text{ to } 5$
2) Permeability sufficient to prevent the buildup of large seepage forces	$\frac{D_{15} \text{ (filter)}}{D_{15} \text{ (soil)}} > 4 \text{ to } 5$
3) Approximately parallel grain size curves	$\frac{D_{50} \text{ (filter)}}{D_{50} \text{ (soil)}} \leq 25$

^a D_x = diameter such that x percent of material is finer.

^b filter = layer above, soil = layer below.

Source: 25,154.

TABLE 36. COLUMN MATERIALS GRADING ANALYSIS

Filter Soil	Limestone	Dolomite	#16 Silica Sand	#60 Silica Sand	P-Gravel	Coal	Claystone 4:1	Granite Bedrock 1:1	Granite Bedrock 3:1
Limestone			2 Marg. ^{a,b}	2		2 Marg.	2		
Dolomite			2 Marg.	2	1		2		
#16 Silica Sand	2	2		2	o.k.	2		2	2
#60 Silica Sand	2	2 Marg.	2 Marg.		1,3	2 Marg.		2 Marg.	3
P-Gravel	2	2	2	2		2			
Coal	2		2 Marg.	2	o.k.		2		
Claystone 4:1				o.k.					
Granite Bedrock 1:1			2 Marg.	2	o.k.				
Granite Bedrock 3:1			2	2	o.k.				

^a Numbers indicate grading analysis criteria definition shown in Table 34 .^b Marg. = Marginal .

Most of the column fill materials were usable when delivered. However, due to the impervious characteristics of the extremely fine-grained claystone, it appeared that a 100 percent claystone layer would not permit leachate drainage. Permeability tests were performed on several different sand to clay mixtures. The mix that provided a reasonable permeability check had about a 3:1 by weight ratio of #60 mesh silica sand to clay. Homogeneous mixing was done in 5 to 10 kg quantities which were more easily handled. The granite material also required mixing in a ratio of 3:1 granitic pea gravel to decomposed granite by weight to achieve the desired permeability.

The top soils used in the soil columns represented common agricultural disposal environments; samples were obtained in the field according to the desired classification and the local in-situ locations were established from the USDA-Soil Conservation Service report Soils of the Malibu Area. Silty clay loam from the Castaic series was selected for the silty loam test soil type. Clay from the Cropley series was used for the clay loam test soil, and very fine sandy loam from the Huerfuerio series for the sandy loam test soil. Table 37 shows the soil characteristics and Figure 23 indicates the locations from which these representative soil samples were obtained.

The silty and clay loams were admixed with #60 mesh silica sand to achieve satisfactory leachate drainage. A 4:1 sand-to-soil mixture by weight was used. The clean silica sand admixtures were used as a permeable, relatively inert "filler," which allowed leachate movement through the simulated sub-surface environment.

The sanitary landfill materials were mixed according to the refuse percentages shown in Table 38, following typical "as disposed" quantities. The "as mixed" percentages varied slightly, and are shown in Table 39.

Column Filling

The columns were filled with materials to simulate various strata in the quantities shown in Table 40 and according to the depths established during the literature search (Figures 15 to 21). Care was taken to add the bottom pea gravel layer slowly to avoid damage to the columns' bottom filter and screen. Column interface level depths were measured with a weighted string held from the top or through an observation port. The placed layers were checked to ensure that there was a level thickness from the center of the column to the circumference.

During column filling the leachate collection lysimeters were placed as shown in Figure 24, with the lysimeter generally located in the layer above the collection tube opening. Filling of material was stopped just below the opening and the lysimeter lowered on a nylon string. The tube was threaded through the hole, and a rubber stopper was placed on the tube and secured in the hole. The height of the lysimeter was adjusted with the string which was then tied to a bar across the top of the column. Column filling was then resumed. When the lysimeters were covered to a depth of 15 cm or more, the string was cut.

TABLE 37. TEST COLUMN SOILS CHARACTERISTICS

Series	Horizon (cm)	Characteristics
Castaic Clay Loam Soil	A 0 - 25	Dry color grayish-brown or light brownish-gray to light yellowish-brown or light olive-brown. Textures are silty clay loam. Noncalcareous with reactions from slightly acid to moderately alkaline. Moderate fine granular structure; hard, sticky, and plastic.
	B 25 - 71	Dry color very pale brown or pale yellow to yellow and light olive brown. Textures similar to horizon A with up to 30 percent (by volume) shale fragments. Calcareous with reactions from neutral to moderately alkaline. Weak fine granular structure; hard, sticky, and plastic.
Cropley Silty loam Soil	A 0 - 36	Dry color of dark gray and very dark gray. Textures of clay to silty clay. Reaction is neutral to mildly alkaline. Medium angular blocky structure; very hard, very sticky, and very plastic.
	B 36 - 96	Colors are dark gray, gray, dark grayish-brown, grayish-brown, olive-brown, and yellowish-brown. Texture ranges from clay to clay loam. Calcareous in the lower section, with reaction from mildly to moderately alkaline. Coarse angular blocky structure; very hard, very sticky, and very plastic.
Huerhuero Sandy loam Soil	A 0 - 10	Colors are grayish-brown, light brownish-gray, pale brown, and brown. Textures are fine sandy loam to loam. Reaction is medium acid to neutral. Fine granular massive structure; slightly hard, non-sticky and non-plastic.
	B 10 - 64	Colors are dark brown, dark yellowish-brown, brown and strong brown. Texture is sandy clay to clay, with up to 15 percent gravels in the lower portion. Reaction is neutral to moderately alkaline and calcareous in the lower portion. Medium to coarse angular blocky structure; very hard, slightly sticky, and slightly plastic.

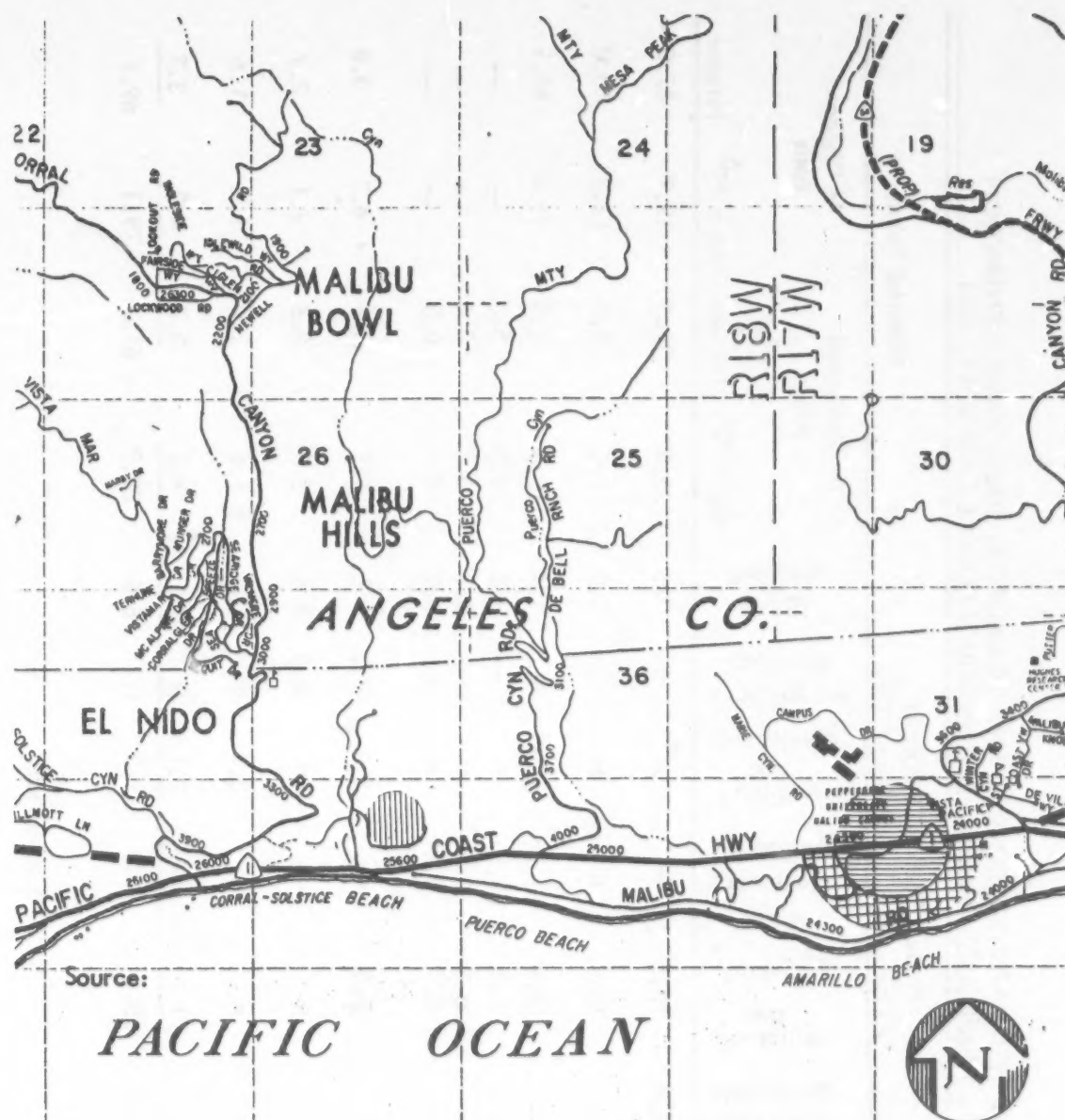


Figure 23. Original location of representative soil samples.

TABLE 36. ESTIMATED RESIDENTIAL AND COMMERCIAL SOLID WASTE GENERATION
BY KIND OF MATERIAL AND PRODUCT SOURCE CATEGORY, 1971

Materials	Product Source Categories "As Generated" Basis (kkg x 10 ⁶)										Material Totals		
	Newspapers, Books and Magazines	Containers and Packaging	Major Household Appliances	Furniture and Furnishings	Clothing and Footwear	Other Products	As Generated Basis kkg x 10 ⁶	Percent	kkg x 10 ⁶	Percent	As Disposed Basis		
Paper	9.3	18.5	--	tr ^a	tr	7.6	35.5	31.3	42.9	37.8			
Glass	--	10.1	tr	tr	--	0.9	11.0	9.7	11.3	10.0			
Metals	--	5.5	1.7	0.1	tr	3.4	10.8	9.5	11.4	10.1			
Ferrous	--	4.9	1.5	tr	--	3.2	9.6	8.5	--	--			
Aluminum	--	0.5	0.1	tr	--	0.1	0.7	0.6	--	--			
Other non-ferrous	--	0.1	0.1	tr	--	0.2	0.4	0.3	--	--			
Plastics	tr	2.3	--	0.1	0.2	1.2	3.8	3.4	4.3	3.8			
Rubber and leather	--	tr	--	tr	0.5	2.4	3.0	2.6	3.1	2.7			
Textiles	tr	tr	--	0.5	0.5	0.6	1.6	1.4	1.8	1.6			
Wood	--	1.6	--	2.1	tr	0.5	4.2	3.7	4.2	3.7			
Non-food product totals	9.3	38.0	1.9	2.9	1.1	16.6	69.9	61.7	79.1	69.7			

(Continued)

TABLE 38 (Cont.)

Materials	Product Source Categories "As Generated" Basis (kg x 10 ⁶)										Material Totals	
	Newspapers, Books and Magazines	Containers and	Packaging	Major Household Appliances	Furniture and Furnishings	Clothing and Footwear	Other Products	As Generated Basis kg x 10 ⁶	Percent	kg x 10 ⁶	As Disposed Basis	Percent
Food waste								20.0	17.6	16.1		14.2
Product totals								89.9	79.3	95.2		83.9
Yard waste								21.9	19.3	16.5		14.6
Miscellaneous inorganics								1.6	1.4	1.7		1.5
Total waste								113.4	100	113.4		100

a Tr= Trace

TABLE 39. SANITARY LANDFILL TEST COLUMN-AS MIXED

Materials	Kg	Percent	Description
Paper	8.39	37.7	Shredded newspaper and shredded paper.
Glass	2.27	10.2	Broken bottles, colored and clear.
Metals	2.15	9.7	Cut-up tin cans, cans and cut wire.
Plastics	0.86	3.9	Shredded plastic trash bags and miscellaneous plastics from trash.
Rubber and Leather	0.59	2.7	Cut-up shoes.
Textiles	0.23	1.0	Shredded drapes and rags.
Wood	<u>0.77</u>	<u>3.5</u>	Cut-up wood crates.
Non-Food Product Total	15.26	68.7	
Food Waste	<u>3.18</u>	<u>14.3</u>	Miscellaneous household food waste.
Product Total	18.44	83.0	
Yard Waste	3.40	15.3	Miscellaneous yard waste.
Miscellaneous Inorganics	<u>0.39</u>	<u>1.7</u>	River gravel and silica sand.
Total	22.23	100.0	

TABLE 40. MATERIALS IN TEST COLUMN LAYERS BY WEIGHT

Column Layers in Order of Addition	Average Weight per Layer by Column Type (kg)							
	Limestone Quarry	Dolomite Quarry	Ocean Disposal	Sanitary Landfill	Coal Mine	Sandy Loam	Clay Loam: sand 1:4	Silty Loam sand 1:3
Pea gravel (.95 cm)						11.3	11.3	11.3
Pea gravel (.64 cm)	12.2 ^a	12.2 ^a	12.2 ^a	12.2 ^a	12.2 ^a	6.4	6.4	6.8
Silica sand #16	5.4	5.4	5.4	5.4	5.4			
Silica sand #60	27.2	27.2	97.7		13.2			
Clay: #60 sand 1:4	22.2	22.2						
Limestone	50.3				25.9			
Dolomite		43.1						
Granite p-gravel: decomposed granite 3:1				34.9				
Silica sand #16				6.4				
Silica sand #60	4.1	4.1		16.8	4.1			
Clay: #60 sand 1:4				14.1	23.6			
Solid waste				12.2				
Bituminous coal					17.2			
Soil horizon B						80.5	88.9	76.9
Soil horizon A						17.9	15.0	12.5
Silica sand #16				8.2	5.4			

^a Columns 21-30 contain 6.8 kg of 0.95 cm gravel covered by 5.4 kg of 0.64 cm gravel.

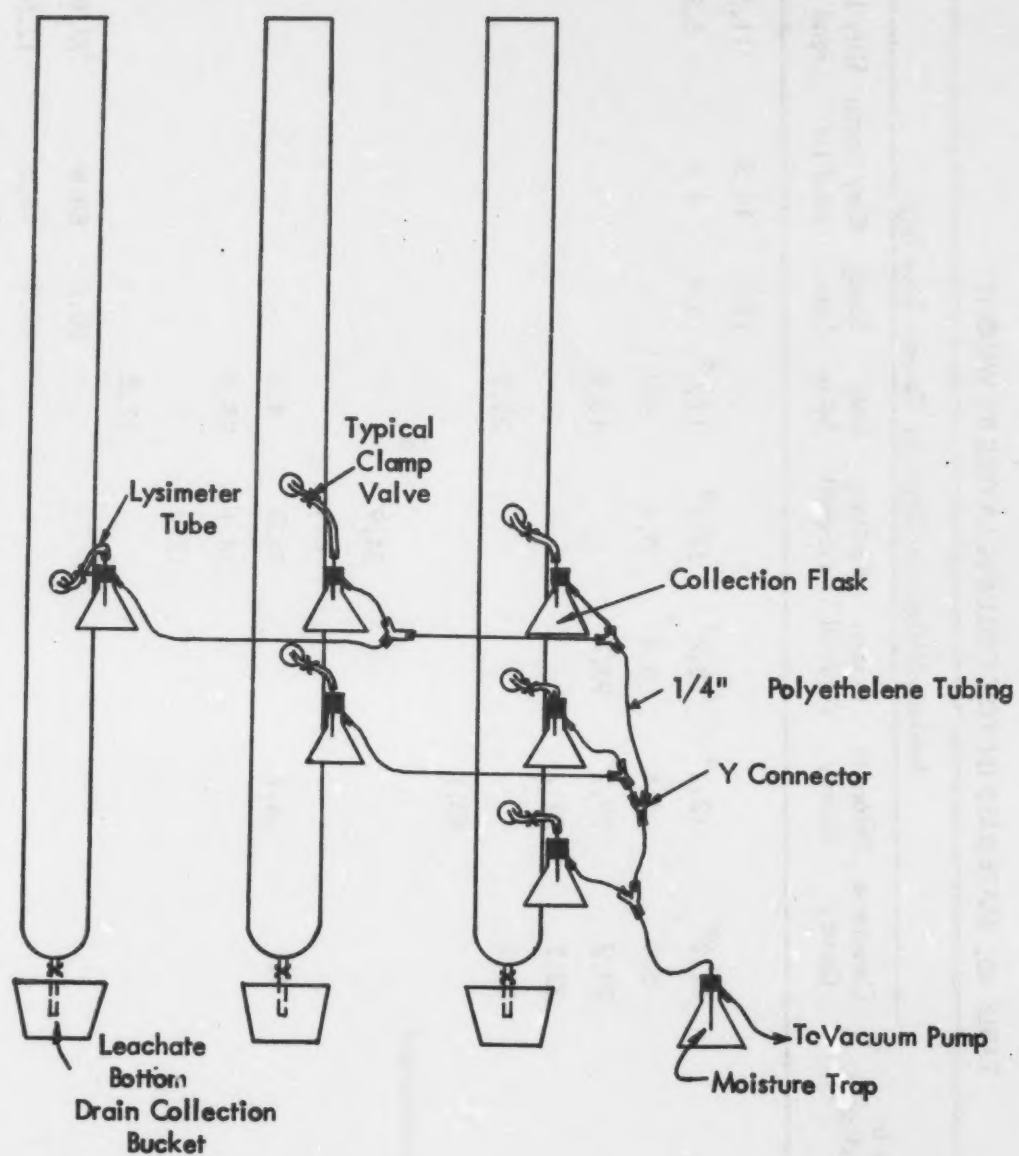


Figure 24. . Typical test column leachate collection system schematic.

For the soils test columns, the leachate lysimeters were left attached to the string for several days while the columns were washed with tap water and the simulated strata compacted. A detailed diagram of the lysimeter construction and placement is given in Figure 24. After filling the test columns, the external leachate collection tubing and flasks, connectors and manifold were added, as shown in Figure 25.

Sample Bottle Labeling

Each lysimeter had its own sample collection flask, labeled with the appropriate identifying column number and lysimeter letter. All lysimeters, drains, and columns were identified sequentially from the bottom of the column up, starting with A as the bottom drain for all the columns. Leachate sample collection bottles were placed and labeled as follows in the typical example:

Column number, column abbreviation, lysimeter letter, and lysimeter location =

2 LQ-C-top lysimeter

Column Washing

Before adding the residues, the strata materials in each column were leached with tap water to ensure washed compacted strata and to establish the base-line column leachate quality and flow quantity. Tap water was added daily for at least two weeks, or until the chemical analysis revealed a nearly constant or zero level of leached constituents. Results of the baseline analyses are given in Figures 32 - 196. To determine the flow rate characteristics of each column, the drains were kept open for two days until there was no further leachate flow into the drain. 7.6 liters of tap water were added at the top, and the rate of water leached for each time period was measured over a period of 27 to 30 hours. In column 14, the residue solidified, in situ, and the water was perched over the top layers. This column was repacked with a sand mixture to eliminate the percolation obstruction. All the columns were successful in percolating water. The column percolation data are shown in Figures 26-30. Analyses of fresh and sea water used for column washing are shown in Tables 41 and 42. Reduction in percolation rates occurred over the 15 months of leaching.

Residue Preparation and Addition

In laboratory studies, it was found that when some residues reacted with water, a large amount of heat was released. To avoid heat damage to the columns, weighed amounts of residues were first placed in an inert container to which water had been added so as to slake and dissipate the heat of reaction. Filter paper (20.3 cm diameter, #1 qualitative) was placed in the columns above the stratum materials before residue addition. The amounts of fluidized-bed combustion residues added to each column are shown on Table 43.

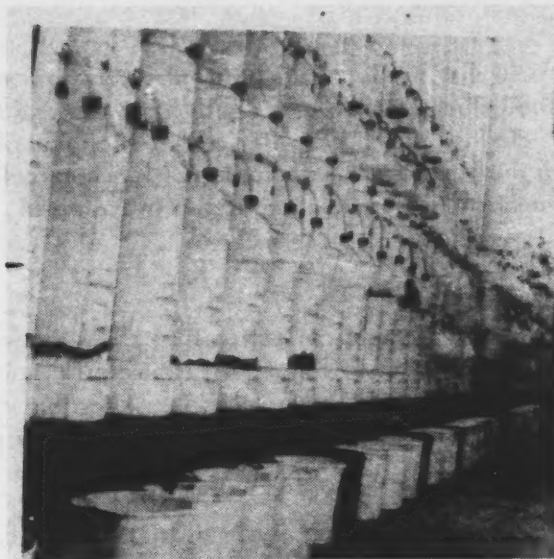


Figure 25. Outdoor columns leachate sampling apparatus.

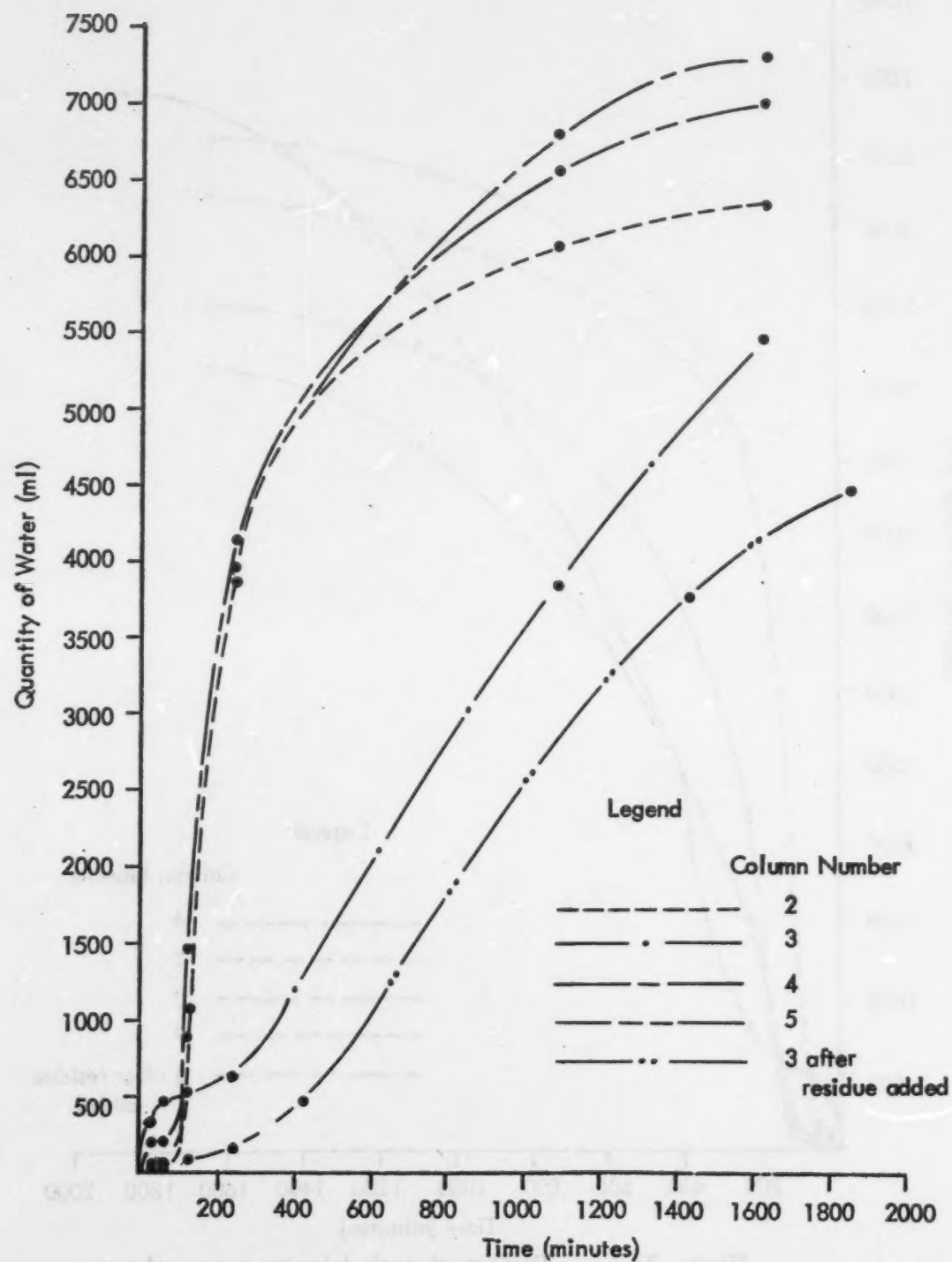


Figure 26 . Drainage through limestone quarry columns.

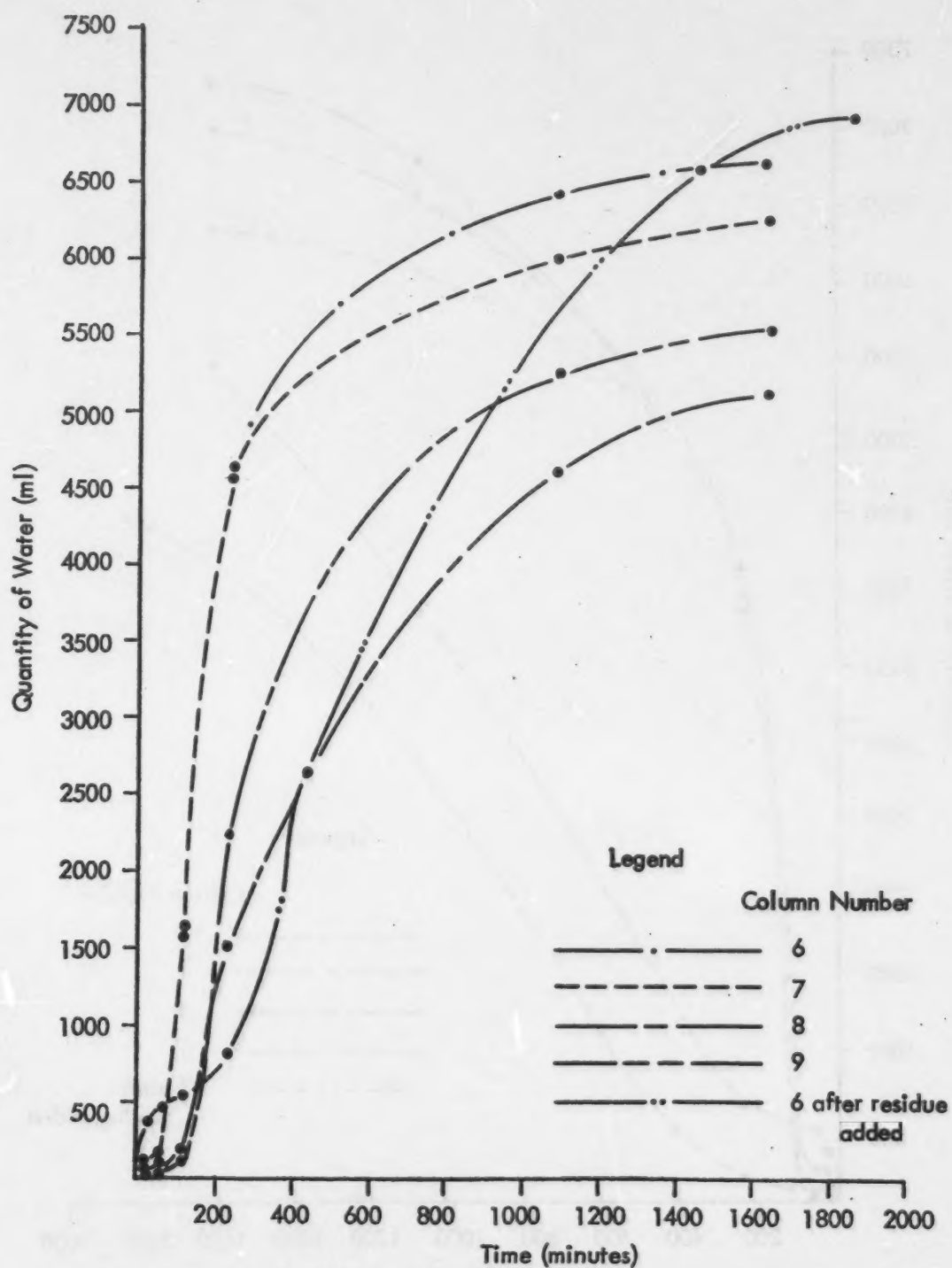


Figure 27 . Drainage through dolomite quarry columns.

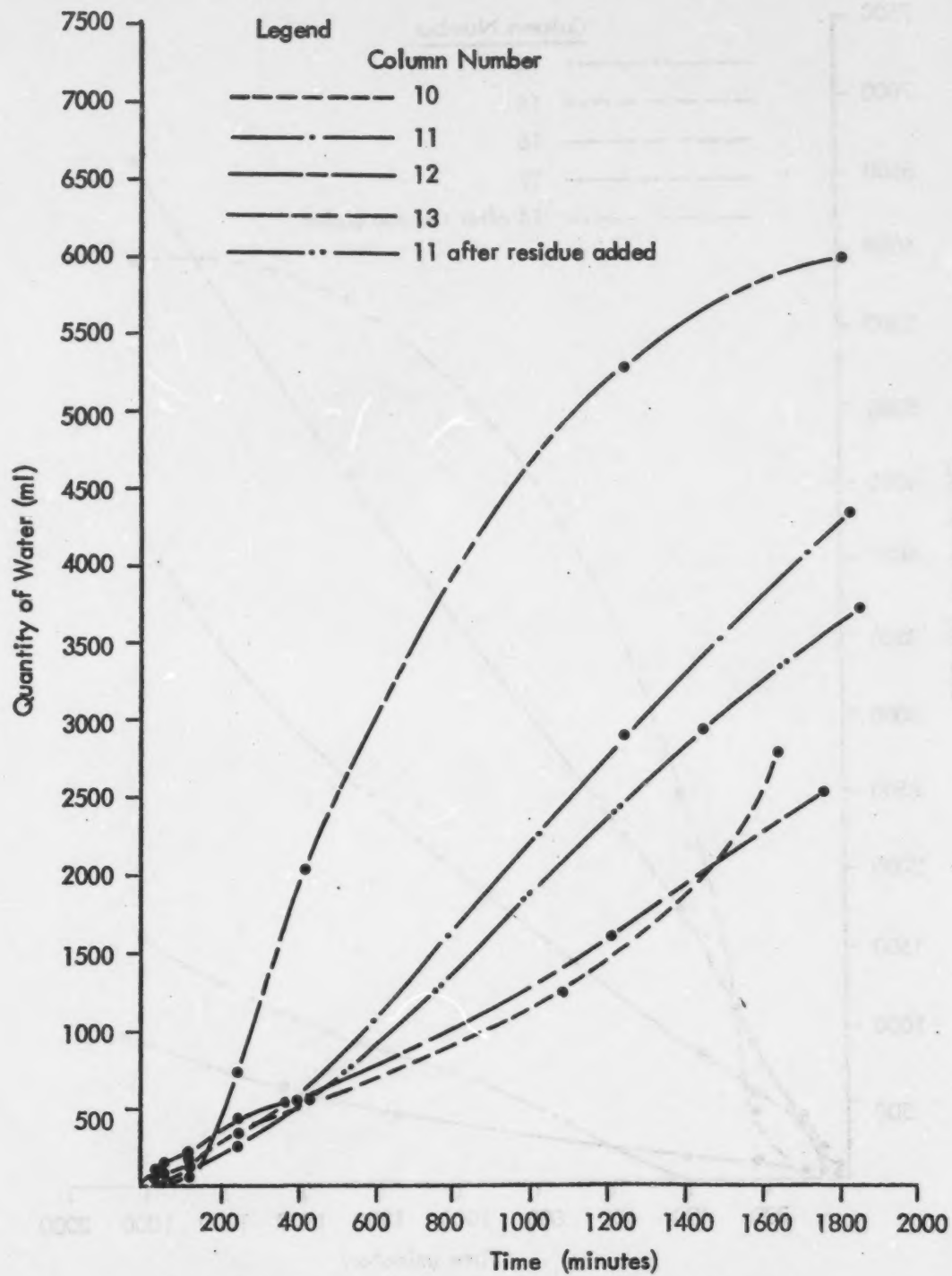


Figure 28. Drainage through sanitary landfill columns.

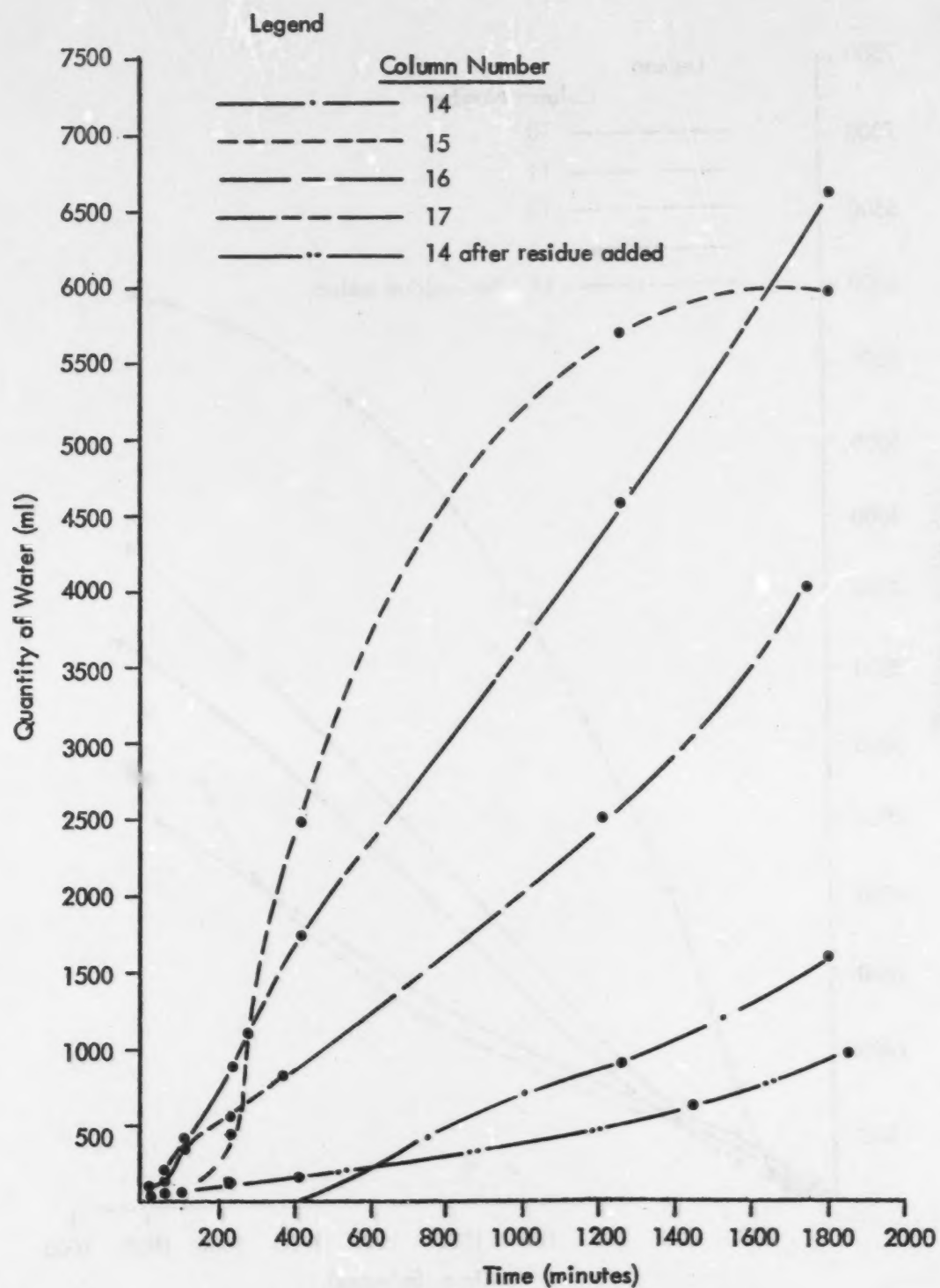


Figure 29 • Drainage through coal mine columns.

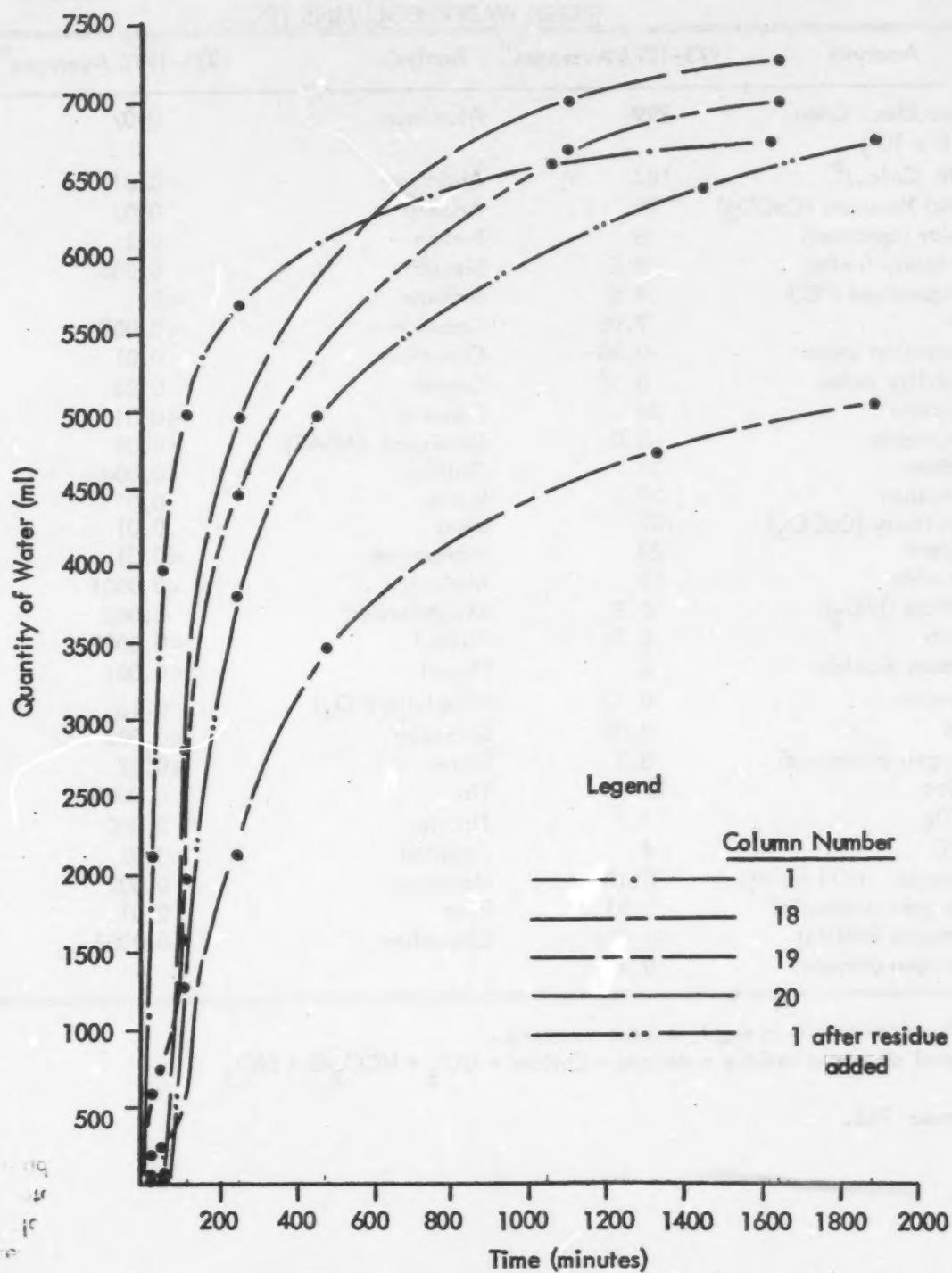


Figure 30 . Drainage through ocean disposal columns.

TABLE 41. COMPLETE ANALYSIS OF LOS ANGELES OWENS RIVER AQUEDUCT
(FRESH WATER) COLUMNS TEST

Analysis	1975-1976 Averages ^a	Analysis	1975-1976 Averages ^a
Spec.Elec. Cond. (K x 10 ⁶)	299	Aluminum	0.07
TDR (Calc.) ^b	184	Antimony	<0.01
Total Hardness (CaCO ₃)	79	Arsenic	0.02
Color (apparent)	8	Barium	0.1
Turbidity (units)	3.2	Bismuth	0.003
Temperature (°C)	14.5	Bromide	<0.1
pH	7.95	Cadmium	<0.002
Saturation index	-0.30	Chromium	0.01
Stability index	8.55	Copper	0.06
Calcium	24	Cyanide	<0.01
Magnesium	5.0	Detergents (MBAS)	<0.05
Sodium	30	Gallium	<0.0002
Potassium	32	Iodide	0.01
Alkalinity (CaCO ₃)	109	Lead	0.01
Sulfate	20	Manganese	<0.01
Chloride	13	Mercury	<0.0001
Nitrate (NO ₃)	0.8	Molybdenum	0.005
Boron	0.34	Nickel	<0.0009
Carbon dioxide	3	Phenol	<0.001
Fluoride	0.52	Phosphate (PO ₄)	0.16
Iron	0.09	Selenium	<0.002
Oxygen (dissolved)	8.9	Silver	<0.02
Silica	22	Tin	0.0005
BOD ₅	1.7	Titanium	0.002
COD	4	Tungsten	<0.07
Nitrogen, TKN (as N)	0.10	Vanadium	0.002
Nitrogen (ammonia)	<0.01	Zinc	0.01
Nitrogen (nitrite)	<0.001	Zirconium	<0.0003
Nitrogen (nitrate)	0.18		

^aChemical results in mg/l, except as noted.

^bTotal dissolved residue = Anions + Cations + CO₃ + HCO₃⁻/2 + SiO₂.

Source: 185.

TABLE 42. SEA WATER ANALYSIS
A. GENERAL: DITMAR'S VALUES FOR THE MAJOR CONSTITUENTS, 1940¹
(Values in Grams Per Kilogram, ⁰/100)

Constituent	1940 Values	
	Cl = 19 ⁰ /00	%
Chlorine	18.980	55.04
Bromine	0.065	0.19
Sulfate	2.649	7.68
Carbonate	0.071	0.21
Bicarbonate	0.14	0.41
Fluorine	0.001	0.00
Boric Acid	0.026	0.07
Magnesium	1.272	3.69
Calcium	0.400	1.16
Strontium	0.013	0.04
Potassium	0.380	1.10
Sodium	10.556	30.61
Total	34.553	

B. PARTIAL ANALYSES OF COLUMNS TEST SEA WATER

Constituent	1975-1976 Averages	
	Cl = 19 ⁰ /00	%
Sulfate	.0032	.00931
Iron	.00052	.0015
Zinc	.00003	.0001
Nickel	.001	.003
Mercury	.0000105	.00003
Lead	.00044	.0013

¹ Source 190.

TABLE 43. RESIDUES ADDED TO COLUMNS

Residue Type	Quantity Added (kg)	Remarks
Pope, Evans, & Robbins Virginia Fly Ash	9.07	slaked with 3.8 l water over two days.
Pope, Evans, & Robbins Virginia Spent Bed Material	13.61	unslaked weight.
Exxon Miniplant New Jersey Fly Ash	13.61	unslaked weight.
Exxon Miniplant New Jersey Spent Bed Material	9.98	slaked with 7.6 l water over two days, slaked (dry) weight. Equivalent unslaked weight, 8.7 kg.
Esso Gasifier Plant England Fly Ash	11.34	slaked with 3.8 l water over one day, unslaked weight.
Esso Gasifier Plant England Spent Bed Material	6.35	slaked with 3.8 l over one day, unslaked weight.

Water Addition

Tri-weekly (every Monday, Wednesday, and Friday afternoons), potable water was added to all columns, except for the ocean disposal columns which received sea water. All clamps on drains were closed before the fresh or sea water was added, and the water was retained in the columns through the next sampling day. Ideally, 7.6 liters of water were added each time. However, some columns gradually reduced their drainage after several months so that they received less than 7.6 liters at the top of the column. Procedures for the sea water columns were changed after six months to investigate leaching in a flooded environment; i.e., the sea water columns were kept saturated except for partial surface drainage which allowed the addition of fresh sea water. The purpose of the flooding test was to simulate the addition of a residual landfill into an ocean environment rather than in the former tidal prism environment.

Leachate Sampling

Leachate samples from the column drains and lysimeters were collected to measure the results of the previous day's water addition. See Table 44 for discussion of ocean water test column procedures. Every Monday morning, sampling was started after emptying the lysimeter collection flasks containing weekend drainage. With a vacuum pump set at a vacuum of about 1,760 cm of water, 5 to 6 hours of collecting time normally provided sufficient sample for analysis. All column lysimeters were sampled simultaneously using the interconnected tubing and flask systems linked to the vacuum pump (See Figure 24 above).

After the vacuum pump was started, a collection container was placed beneath each drain tube and the drain valve was opened. At the end of the day, the amount collected in the container was noted and the sample was taken. Equal amounts of daily samples were composited to make up one weekly sample of 250 ml. If there was insufficient sample at the end of the day, pumping was maintained until the amount needed for analysis was obtained. After sampling all outlet valves for the leachate, drains were closed to prepare for the next water addition.

Next, the leachate containers were rinsed clean with tap water to avoid contamination of the next sample. Notes were made in a daily log regarding routine activities or variations in the usual procedures and noted observations.

Leachate Analysis

The composite samples were analyzed for pH, sulfate, chloride, iron, zinc, nickel, lead, specific conductivity, and total dissolved solids. During the first 25 weeks of column operation, weekly composites were analyzed; thereafter, the frequency of laboratory analysis was reduced to once for each two-week period, and after 32 weeks, to once for each four-week period. See Tables 45 through 51 for results of these analyses and drinking water standards. Figures 31 through 159 give results of studies of leachate versus total volume of water applied. Figures 31 through 143 also show the total grams of constituents in the columns before the leachate sampling was initiated. Figures 160 - 176 illustrate the change in pH with the total volume of water applied.

**TABLE 44. PROCEDURE FOR SAMPLING AND FILLING THE FLOODED
OCEAN WATER TEST COLUMNS**

1. Filled columns initially with ocean water.
 2. Collected leachate samples from opened lysimeters per original procedure (at 8:00 A.M. on Monday, Wednesday, and Friday).
 3. Closed leachate lysimeter valves at 9:00 A.M.
 4. Shut off the leachate valves which provided sufficient sampling amounts.
 5. In the afternoon, refilled the column with the same amount of ocean water as was gravity or vacuum leached.
 6. All other routine compositing and analytical procedures were maintained.
-

TABLE 45. CONSTITUENT REMOVAL BY OCEAN DISPOSAL COLUMN STRATA

Column Layer	Sulfate		Iron		Zinc		Nickel		Mercury		Lead	
	g ^a	% ^b	g	%	g	%	g	%	g	%	g	%
Column 1												
Water	1100		0.540		0.052		0.700		1.500		0.750	
Residue	360		0.950		0.052		0.700		1.500		0.440	
Sandstone (Upper)	360		0.950		0.032	38	0.350	50	1.500		0.440	
Sandstone (Lower)	360		0.500	47	0.032		0.350		1.500		0.440	
Drain		100		53		62		50		100		100
Column 18												
Water	1100		0.540		0.052		0.700		1.500		0.750	
Residue	1000		0.740		0.052		0.700		1.500		0.220	
Sandstone (Upper)	1000		0.740		0.052		0.700		1.500		0.220	
Sandstone (Lower)	1000		0.180	76	0.052		0.700		1.500		0.220	
Drain		100		24		100		100		100		100
Column 19												
Water	1100		0.540		0.052		0.700		1.500		0.750	
Residue	370		0.270		0.052		0.700		1.500		0.150	
Sandstone (Upper)	370		0.270		0.052		0.550	21	1.500		0.150	
Sandstone (Lower)	370		0.240	11	0.052	28	0.550		1.500		0.150	
Drain		100		89		72		79		100		100
Column 20												
Water	1100		0.540		0.052		0.700		1.500		0.750	
Residue	850		0.220		0.047		0.700		1.500		0.150	
Sandstone (Upper)	850		0.220		0.047		0.550	50	1.500		0.150	
Sandstone (Lower)	850		0.220	47	0.034	28	0.550		1.500		0.150	
Drain		100		53		62		50		100		100

^a g = Grams of constituent in leachate leaving column layer (or applied in tap water).^b % = Percent removal of constituent in leachate from residue layer.

TABLE 46. CONSTITUENT REMOVAL BY LIMESTONE QUARRY COLUMN STRATA

Column Layer	Sulfate		Iron		Zinc		Nickel		Mercury		Lead	
	g ^a	% ^b	g	%	g	%	g	%	g	%	g	%
Column 2												
Water	10		0.055		0.002		0.000		0.000		0.000	
Residue	450		0.055		0.027		0.070		0.130		0.042	
Limestone	130	71	0.028	49	0.018	33	0.045	36	0.130		0.042	
Claystone	100	7	0.028		0.018		0.025	- ^c	0.130		0.028	33
Sandstone	100		0.028		0.018		0.025		0.130		0.028	
Drain		22		51		67		9		100		67
Lysimeter loss								55				
Column 3												
Water	10		0.055		0.002		0.000		0.000		0.000	
Residue	375		0.055		0.013		0.084		0.225		0.035	
Limestone	220	41	0.045	18	0.007	46	0.040	52	0.225		0.035	
Claystone	170	13	0.045		0.007		0.040		0.225		0.035	
Sandstone	170		0.045		0.007		0.040		0.225		0.035	
Drain		46		82		54		48		100		100
Column 4												
Water	10		0.055		0.002		0.000		0.000		0.000	
Residue	330		0.055		0.019		0.104		0.370		0.026	
Limestone	280	15	0.027	51	0.009	53	0.054	48	0.370		0.026	
Claystone	280		0.027		0.009		0.054		0.270	37	0.026	
Sandstone	280		0.027		0.009		0.054		0.270		0.026	
Drain		85		49		47		52		63		100
Column 5												
Water	10		0.055		0.002		0.000		0.000		0.000	
Residue	310		0.055		0.013		0.104		0.190		0.032	
Limestone	220	29	0.025	55	0.007	46	0.050	52	0.190		0.032	
Claystone	170	16	0.025		0.007		0.050		0.190		0.032	
Sandstone	170		0.025		0.007		0.050		0.190		0.032	
Drain		55		45		54		48		100		100

^ag = Grams of constituent in leachate leaving column layer (or applied in tap water).^b% = Percent removal of constituent in leachate from residue layer.^c = Difference in quantities is due to removal of constituent in lysimeter leachate, not in column material.

TABLE 47. CONSTITUENT REMOVAL BY DOLOMITE QUARRY COLUMN STRATA

Column Layer	Sulfate		Iron		Zinc		Nickel		Mercury		Lead	
	g ^a	% ^b	g	%	g	%	g	%	g	%	g	%
Column 6												
Water	10		0.055		0.003		0.000		0.000		0.000	
Residue	380		0.055		0.038		0.103		0.145		0.056	
Dolomite	200	47	0.045	18	0.029	24	0.033	68	0.145		0.056	
Claystone	200		0.045		0.017	21	0.033		0.145		0.056	
Sandstone	200		0.045		0.012	— ^c	0.033		0.145		0.056	
Drain		53		82		32		32		100		100
Lysimeter loss						23						
Column 7												
Water	10		0.055		0.003		0.000		0.000		0.000	
Residue	420		0.055		0.023		0.070		0.500		0.050	
Dolomite	320	24	0.038	31	0.013	43	0.036	49	0.500		0.050	
Claystone	180	33	0.038		0.007	26	0.036		0.190	62	0.050	
Sandstone	180		0.038		0.007		0.036		0.190		0.050	
Drain		43		69		31		51		38		100
Column 8												
Water	10		0.055		0.003		0.000		0.000		0.000	
Residue	360		0.055		0.018		0.104		0.270		0.036	
Dolomite	300	17	0.044	20	0.007	61	0.042	40	0.270		0.036	
Claystone	250	14	0.044		0.005	11	0.042		0.240	11	0.025	31
Sandstone	250		0.044		0.005		0.042		0.240		0.025	
Drain		69		80		28		60		89		69
Column 9												
Water	10		0.055		0.003		0.000		0.000		0.000	
Residue	300		0.055		0.019		0.104		0.180		0.018	
Dolomite	150	50	0.044	20	0.008	58	0.047	55	0.180		0.018	
Claystone	150		0.044		0.008		0.047		0.140	22	0.011	39
Sandstone	150		0.044		0.008		0.047		0.140		0.011	
Drain		50		80		42		45		78		61

^ag = Grams of constituent in leachate leaving column layer (or applied in tap water).^b% = Percent removal of constituent in leachate from residue layer.^c = Difference in quantities is due to removal of constituent in lysimeter leachate, not in column material.

TABLE 48. CONSTITUENT REMOVAL BY SANITARY LANDFILL COLUMN STRATA

Column Layer	Sulfate		Iron		Zinc		Nickel		Mercury		Lead	
	g ^a	% ^b	g	%	g	%	g	%	g	%	g	%
Column 10												
Water	10				0.0025		0.000		0.000		0.000	
Residue	330				0.0045		0.105		0.125		0.018	
Landfill	50	85			0.0045		0.032	70	0.125		0.018	
Claystone	50				0.0045		0.024	8	0.095	24	0.013	28
Granite	50				0.0045		0.024		0.095		0.013	
Drain		15				100		22		76		72
Column 11												
Water	10				0.0025		0.000		0.000		0.000	
Residue	370				0.022		0.105		0.200		0.070	
Landfill	160	57			0.022		0.050	52	0.200		0.070	
Claystone	135				0.018	18	0.040	10	0.150	25	0.054	23
Granite	135				0.018		0.040		0.150		0.054	
Drain		36				82		38		75		77
Lysimeter loss		7										
Column 12												
Water	10				0.0025		0.00		0.00		0.000	
Residue	440				0.007		0.10		0.275		0.290	
Landfill	120	73			0.007		0.06	40	0.275		0.290	
Claystone	75	6			0.006	14	0.040 ^c		0.275		0.190	34
Granite	75				0.006		0.040		0.275		0.190	
Drain		17				86		27		100		66
Lysimeter loss		4						33				
Column 13												
Water	10				0.0025		0.0025		0.000		0.000	
Residue	470				0.008		0.065		0.165		0.019	
Landfill	50	89			0.008	38	0.042	20	0.165		0.0195	
Claystone	50				0.005		0.035	11	0.125	24	0.0105	41
Granite	50				0.005	25	0.035		0.125		0.0105	
Drain		11				37		69		76		59

^ag = Grams of constituent in leachate leaving column layer (or applied in tap water).

^b% = Percent removal of constituent in leachate from residue layer.

^c = Difference in quantities is due to removal of constituent in lysimeter leachate, not in column material.

TABLE 49. CONSTITUENT REMOVAL BY COAL MINE COLUMN STRATA

Column Layer	Sulfate		Iron		Zinc		Nickel		Mercury		Lead	
	a	b										
	g	%	g	%	g	%	g	%	g	%	g	%
Column 14												
Water	5		0.055		0.003		0.000		0.000		0.000	
Residue	370		0.055		0.020		0.104		0.190		0.075	
Bitum. coal	180	51	0.035	36	0.020		0.038	63	0.190		0.075	
Claystone	115	18	0.035		0.020		0.038		0.080	58	0.048	36
Limestone	115		0.035		0.012	40	0.026	12	0.080		0.034	8
Sandstone	115		0.035		0.012		0.026		0.080		0.028	— ^c
Drain		31		64		60		25		42		35
Lysimeter loss												21
Column 15												
Water	5		0.055		0.003		0.000		0.000		0.000	
Residue	450		0.055		0.023		0.070		0.125		0.033	
Bitum. coal	225	50	0.023	58	0.023		0.042	40	0.125		0.033	
Claystone	180	10	0.023		0.011	52	0.042		0.090	28	0.033	
Limestone	125	12	0.023		0.004	30	0.028	20	0.090		0.022	33
Sandstone	125		0.023		0.004		0.028		0.090		0.011	**
Drain		28		42		18		40		72		33
Lysimeter loss												33
Column 16												
Water	5		0.055		0.003		0.000		0.000		0.000	
Residue	350		0.055		0.026		0.103		0.135		0.024	
Bitum. coal	250	29	0.030	45	0.026		0.048	53	0.135		0.024	
Claystone	250		0.030		0.026		0.048		0.110	19	0.024	
Limestone	250		0.030		0.007	73	0.038	10	0.110		0.013	46
Sandstone	250		0.030		0.007		0.038		0.110		0.013	
Drain		71		55		27		37		81		54
Column 17												
Water	5		0.055		0.003		0.000		0.000		0.000	
Residue	300		0.055		0.018		0.102		0.180		0.023	
Bitum. coal	200	33	0.022	60	0.018		0.080	22	0.180		0.023	
Claystone	200		0.022		0.018		0.080		0.150	17	0.023	
Limestone	200		0.022		0.005	72	0.040	39	0.150		0.020	13
Sandstone	200		0.022		0.005		0.040		0.150		0.020	
Drain		67		40		28		39		83		87

^a g = Grams of constituent in leachate leaving column layer (or applied in tap water).

^b % = Percent removal of constituent in leachate from residue layer.

^c = Difference in quantities is due to removal of constituent in lysimeter leachate, not in column material.

**TABLE 50 . EPA PROPOSED REGULATIONS ON INTERIM
PRIMARY DRINKING WATER STANDARDS, 1975**

Constituent or characteristic	Value	Reason for standard
Physical		
Turbidity, units	1 ^a	Aesthetic
Chemical, mg/l		
Arsenic	0.05	Toxic
Barium	1.0	Toxic
Cadmium	0.01	Toxic
Carbon chloroform extract	0.7	Toxic
Chromium, hexavalent	0.05	Toxic
Cyanide	0.2	Toxic
Fluoride	1.4-2.4 ^b	Toxic
Lead	0.05	Toxic
Mercury	0.002	Toxic
Nitrates as N	10	Toxic
Selenium	0.01	Toxic
Silver	0.05	Cosmetic
Bacteriological		
Total coliform, per 100 ml	1	Disease
Pesticides, mg/l		
Chlordane	0.003	Toxic
Endrin	0.0002	Toxic
Heptachlor	0.0001	
Heptachlor epoxide	0.0001	Toxic
Lindane	0.004	Toxic
Methoxychlor	0.1	Toxic
Toxaphene	0.005	Toxic
2,4-D	0.1	Toxic
2,4,5-TP	0.01	Toxic

^a Five mg/l may be substituted if it can be demonstrated that it does not interfere with disinfection.

^b Dependent upon temperature: higher limits for lower temperatures.

Source: 162.

TABLE 51 . SURFACE WATER CRITERIA FOR PUBLIC WATER SUPPLIES

Constituent or characteristic	Permissible criteria	Desirable criteria
Microbiological:		
Total coliform	10,000/100 ml ¹	100/100 ml ¹
Fecal coliform	2,000/100 ml ¹	20/100 ml ¹
Inorganic chemicals: (mg/l)		
Ammonia	0.5 (as N)	0.01
Arsenic	0.05	Absent
Barium	1.0	do
Boron	1.0	do
Cadmium	0.01	do
Chloride	250	25
Chromium, hexavalent	0.05	Absent
Copper	1.0	Virtually absent
Dissolved oxygen	4 (monthly mean) 3 (individual sample)	Near saturation
Iron (filterable)	0.3	Virtually absent
Lead	0.05	Absent
Manganese (filterable)	0.05	do
Nitrates plus nitrite	10 (as N)	Virtually absent
pH (range)	5.0-8.5	Narrative
Selenium	0.01	Absent
Silver	0.05	do
Sulfate	250	50
Total dissolved solids (filterable residue)	500	200
Uranyl ion	5	Absent
Zinc	5	Virtually absent
Organic chemicals: (mg/l)		
Carbon chloroform extract (CCE)	0.15	0.04
Cyanide	0.20	Absent
Methylene blue active substances	0.5	Virtually absent
Oil and grease	Virtually absent	Absent
Pesticides:		
Aldrin	0.017	do
Chlordane	0.003	do
DDT	0.042	do
Dieldrin	0.017	do
Endrin	0.001	do
Heptachlor	0.018	do
Heptachlor epoxide	0.018	do
Lindane	0.056	do
Methoxychlor	0.035	do

(continued)

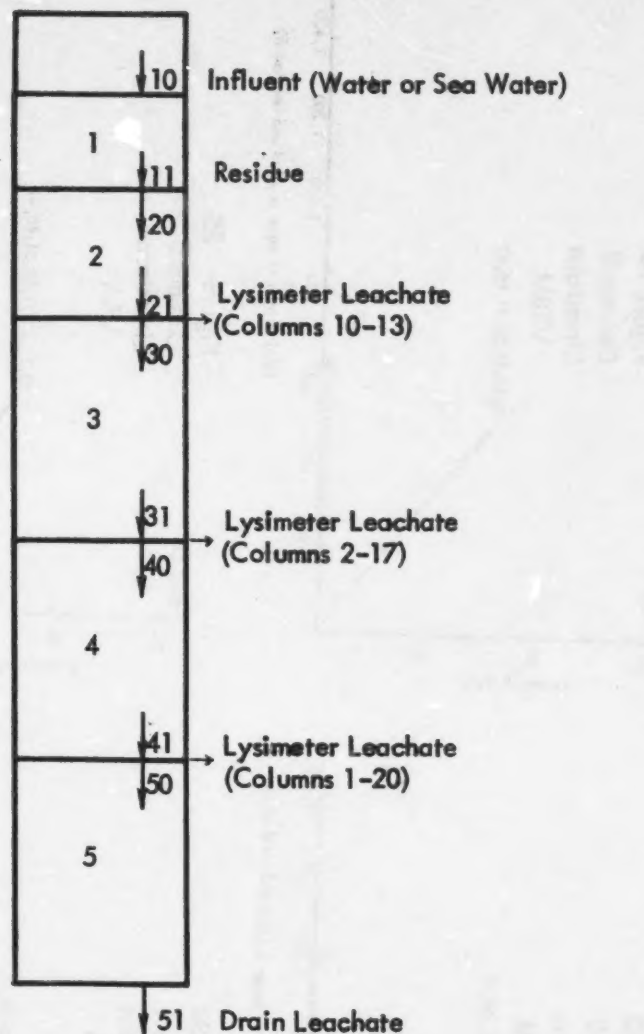
TABLE 51 (continued)

Constituent or characteristic	Permissible criteria	Desirable criteria
Organic chemicals:		
Pesticides: (Cont.)		
Organic phosphates plus carbamates	0.1 ²	do
Toxaphene	0.005	do
Herbicides:		
2,4-D plus 2,4,5-T, plus 2,4,5-TP	0.1	do
Phenols	0.001	do
Radioactivity:		
Gross beta	1,000	100
Radium-226	3	1
Strontium-90	10	2

¹ Microbiological limits are monthly arithmetic averages based upon an adequate number of samples. Total coliform limit may be relaxed if fecal coliform concentration does not exceed the specified limit.

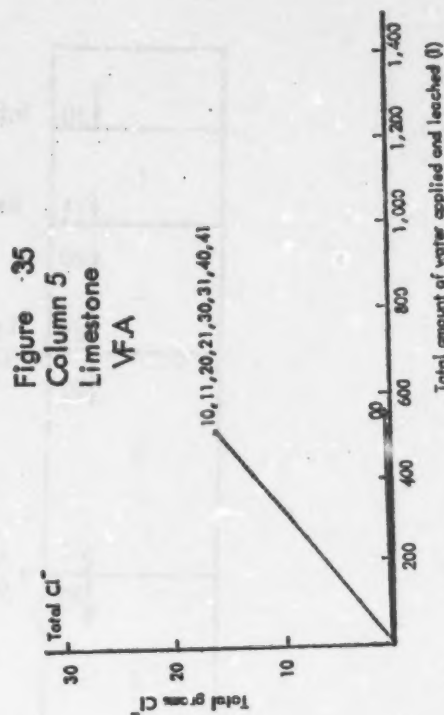
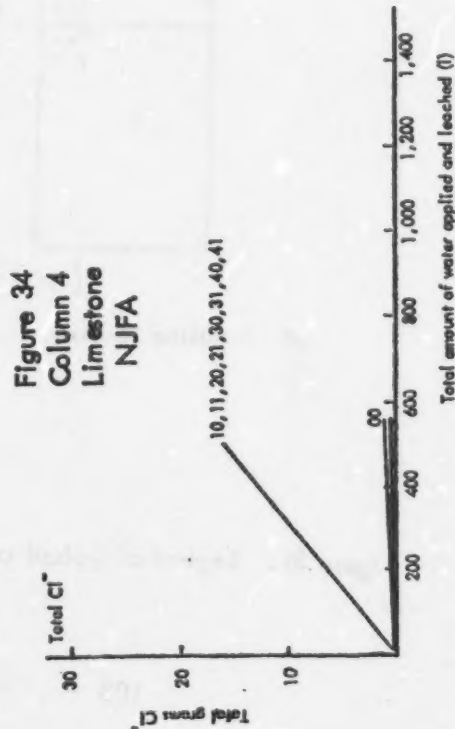
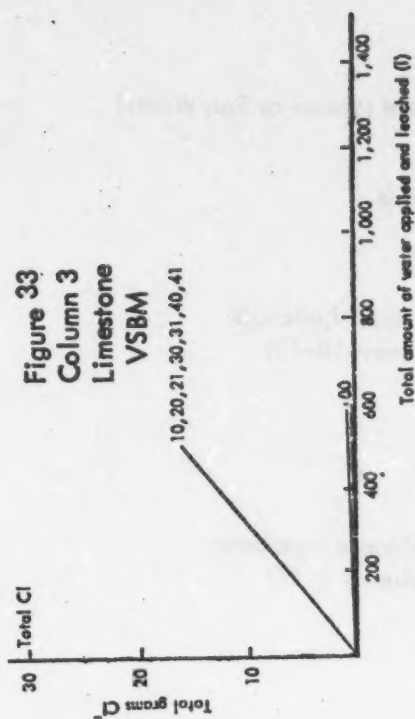
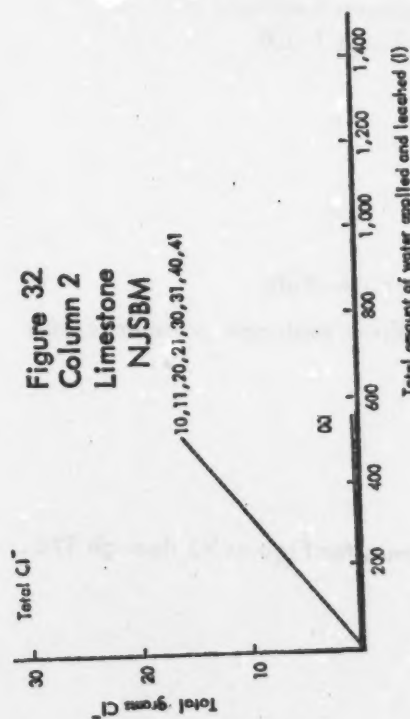
² As parathion in cholinesterase inhibition, it may be necessary to resort to even lower concentrations for some compounds or mixtures.

Source: 72.



00 - Baseline leachate = column drainage without residue

Figure 31. Legend of typical columns for Figures 32 through 176.



Note: See Figure 31 for further legend explanation.

Figures 32 - 35 : Test column leachate cumulative balances: Chloride.

Figure 36
Column 6
Dolomite
VSBM

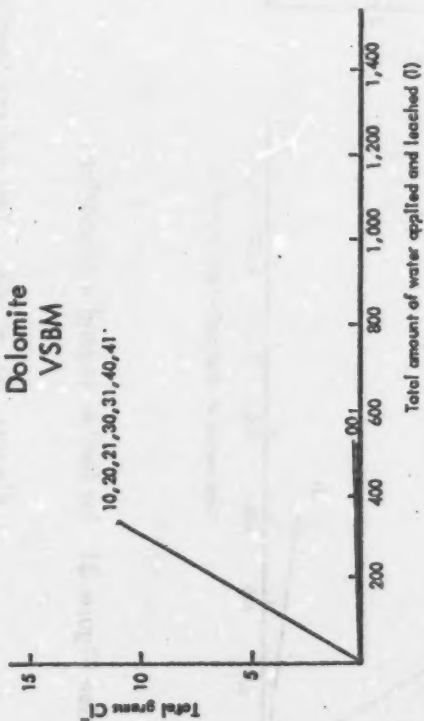


Figure 37
Column 7
Dolomite
NJSBM

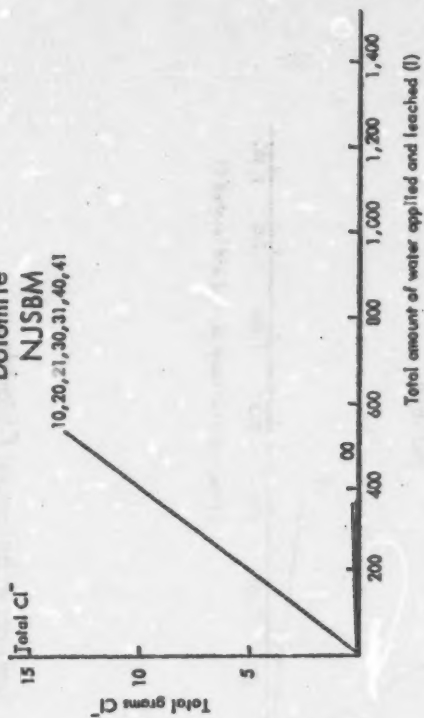


Figure 38
Column 8
Dolomite
VSBM

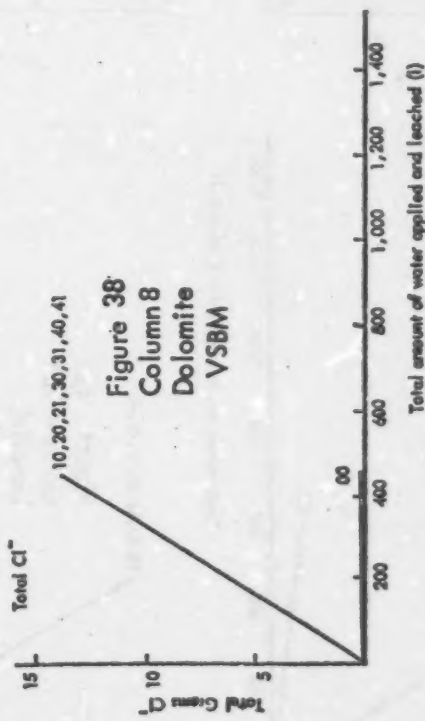
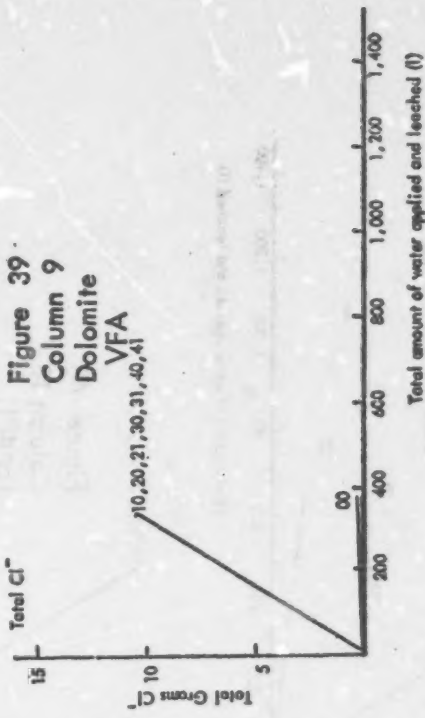
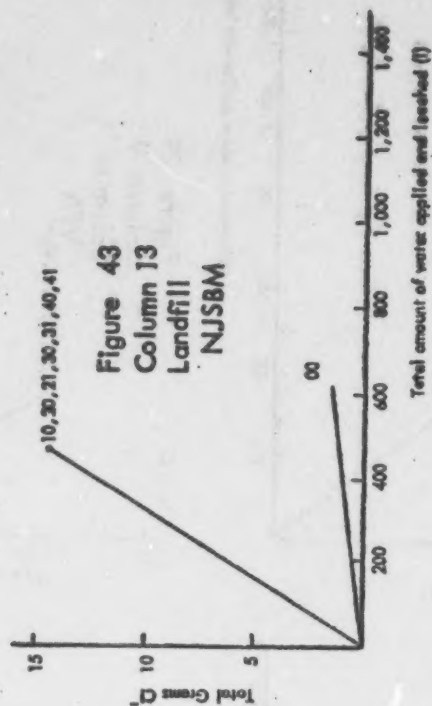
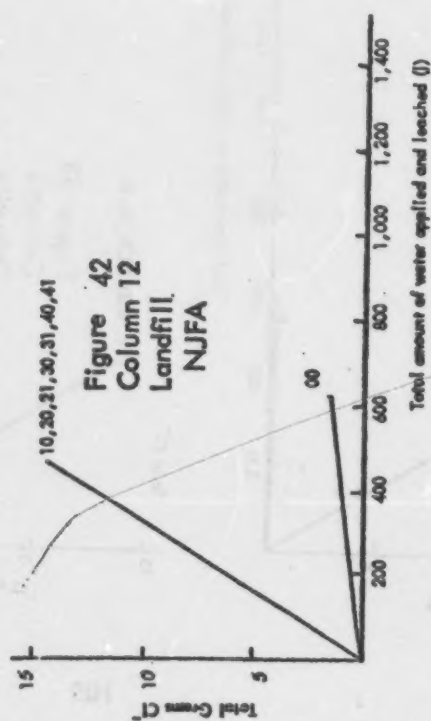
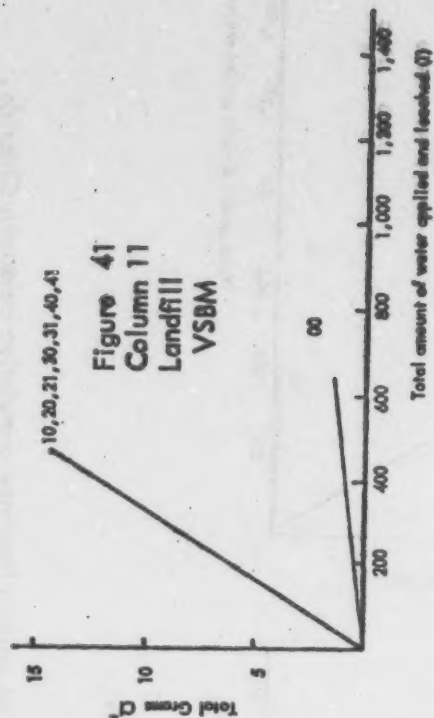
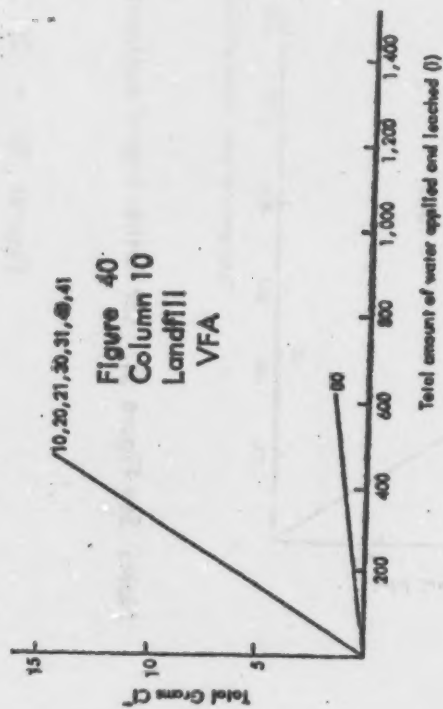


Figure 39
Column 9
Dolomite
VFA



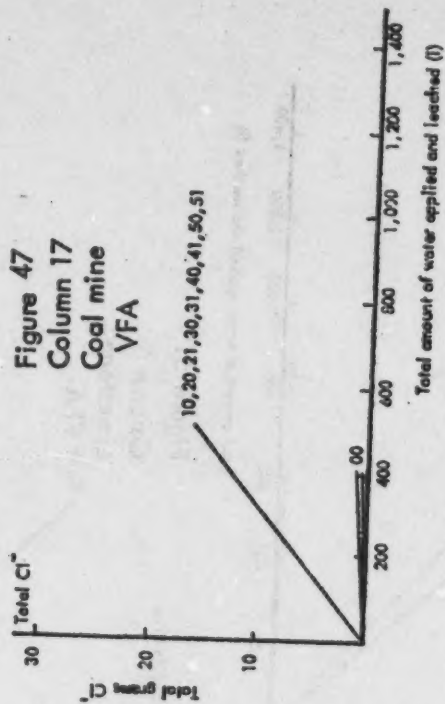
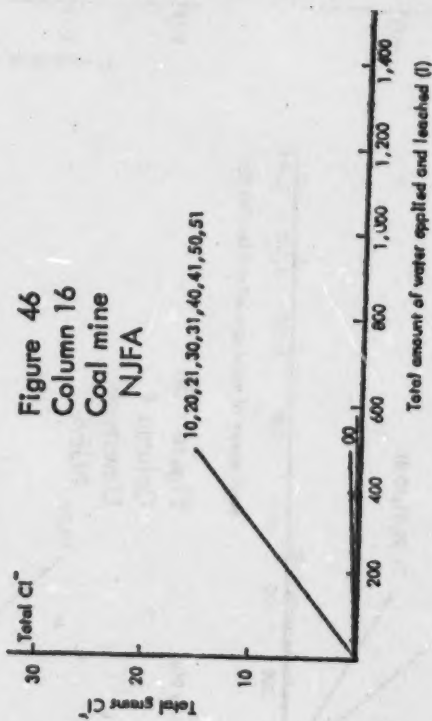
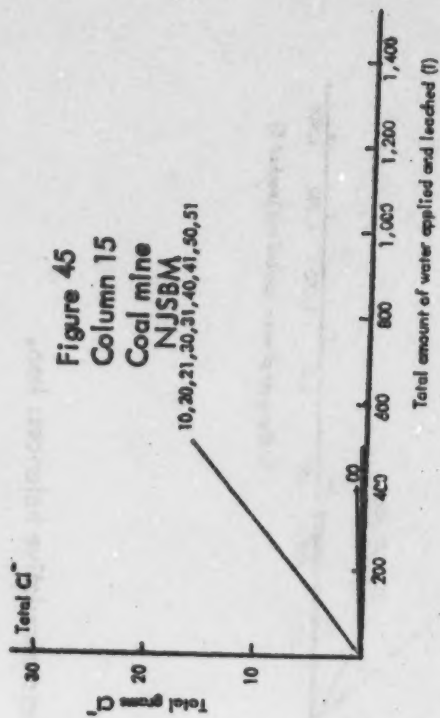
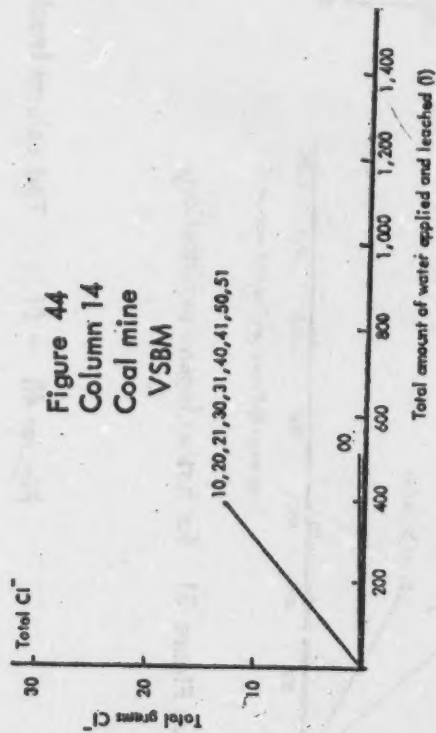
Note: See Figure 31 for further legend explanation.

Figures 36 - 39 . Test column leachate cumulative balances; Chloride.



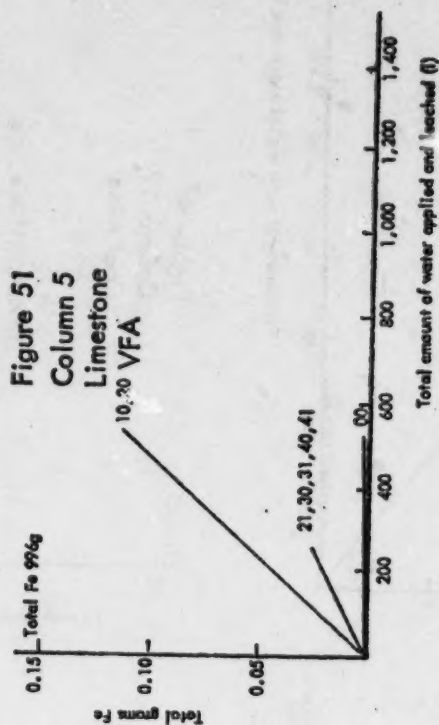
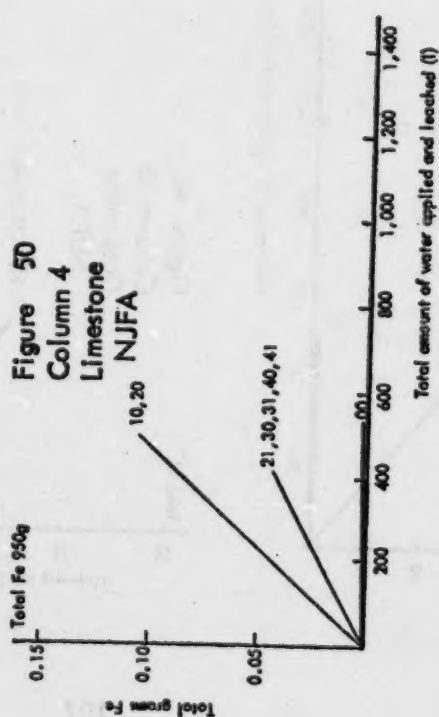
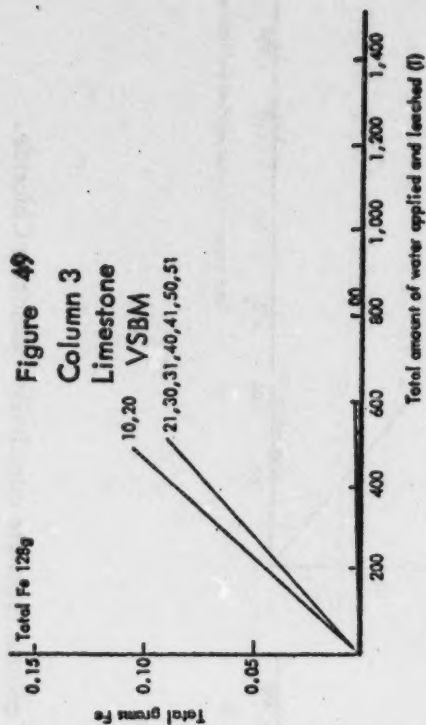
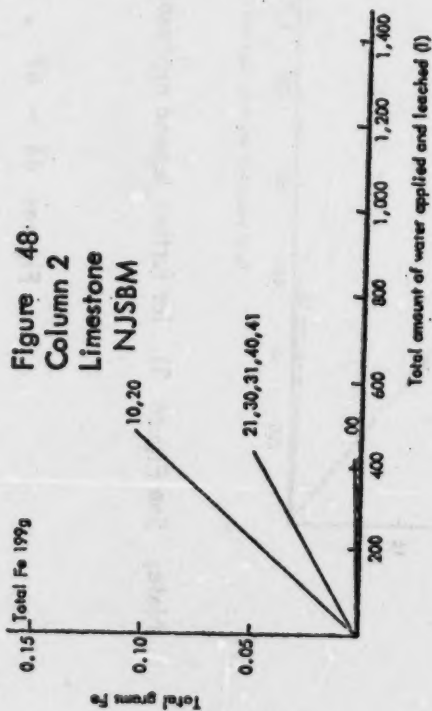
Note: See Figure 31 for further legend explanation.

Figures 40 - 43 . Test column leachate cumulative balances: Chloride.



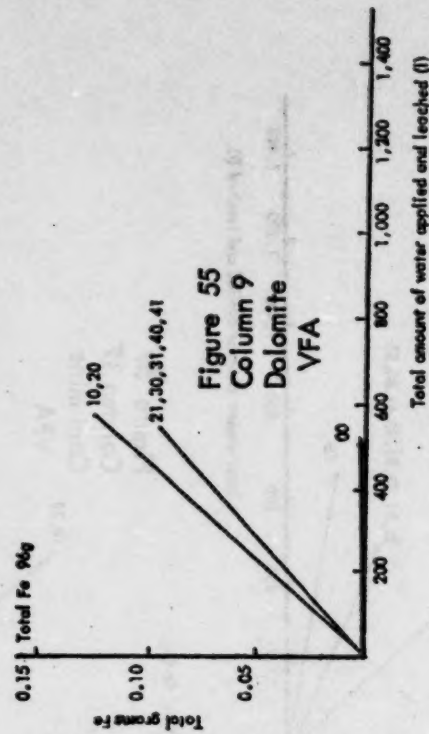
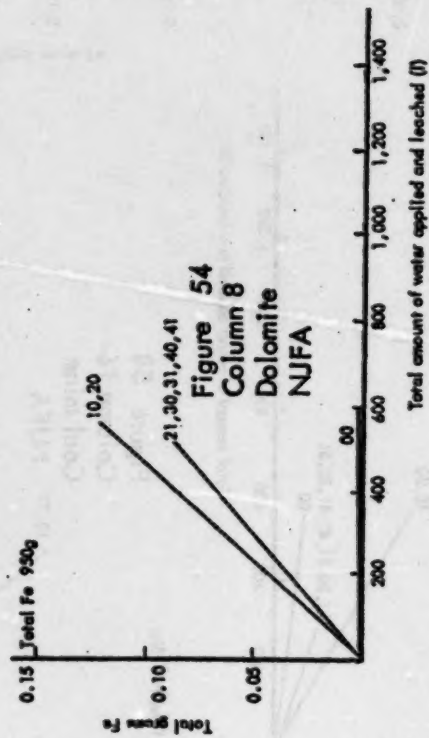
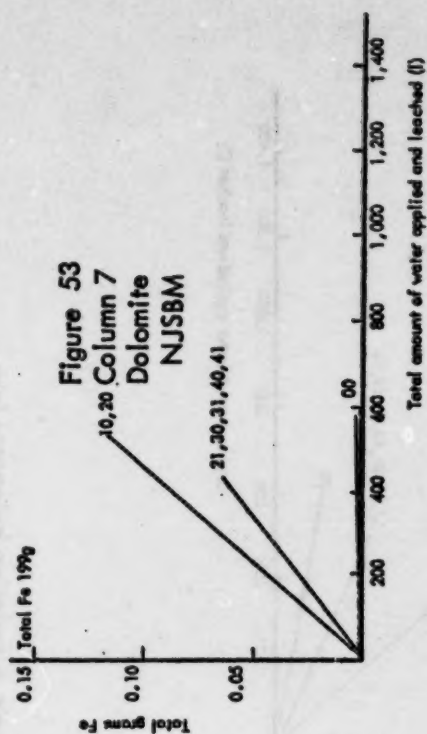
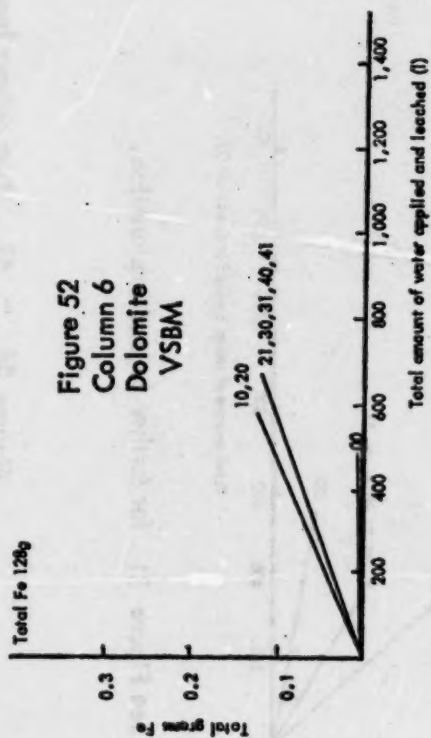
Note: See Figure 31 for further legend explanation.

Figures 44 - 47 . Test column leachate cumulative balances: Chloride.



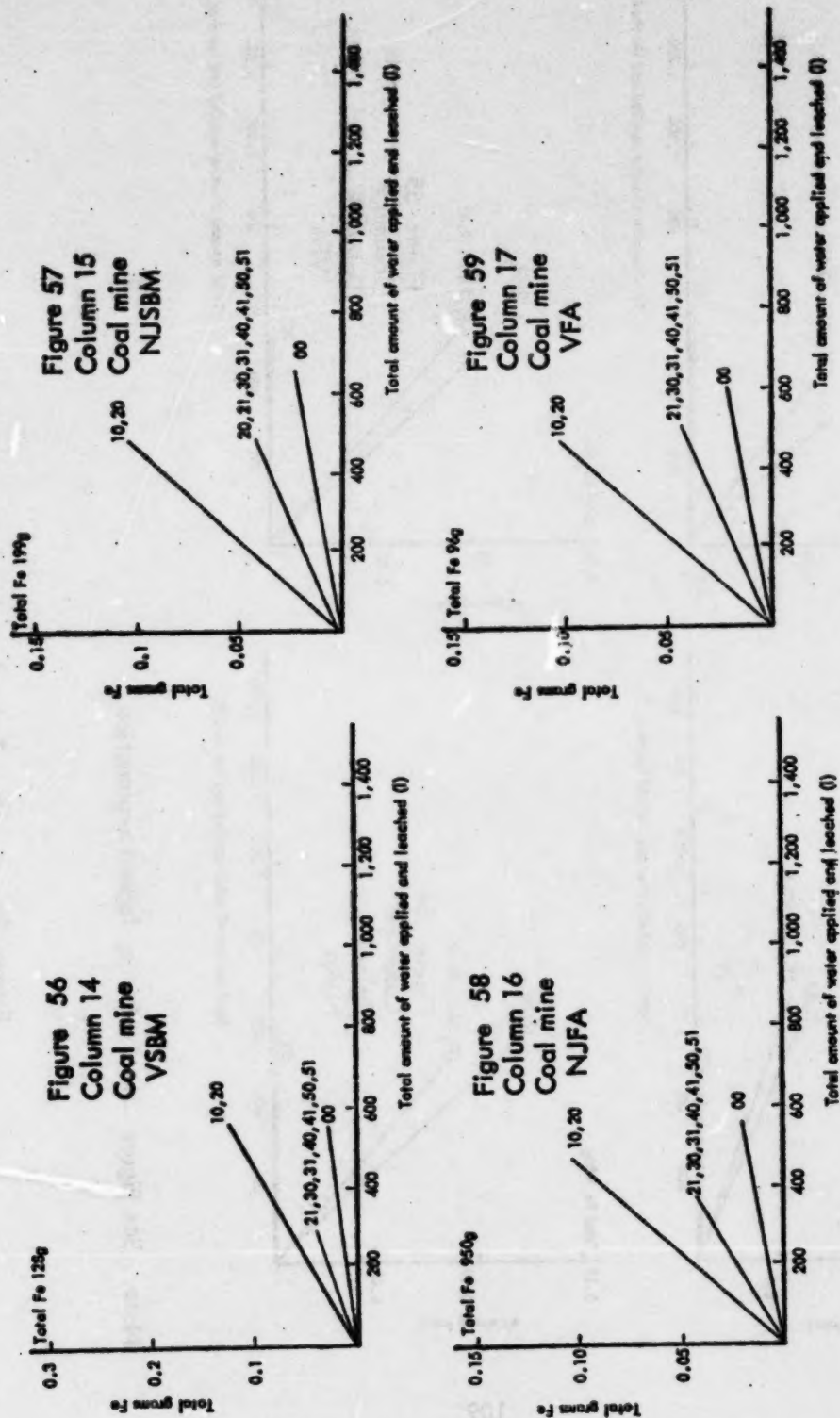
Note: See Figure 31 for further legend explanation.

Figures 48 - 51 . Test column leachate cumulative balances: Iron.



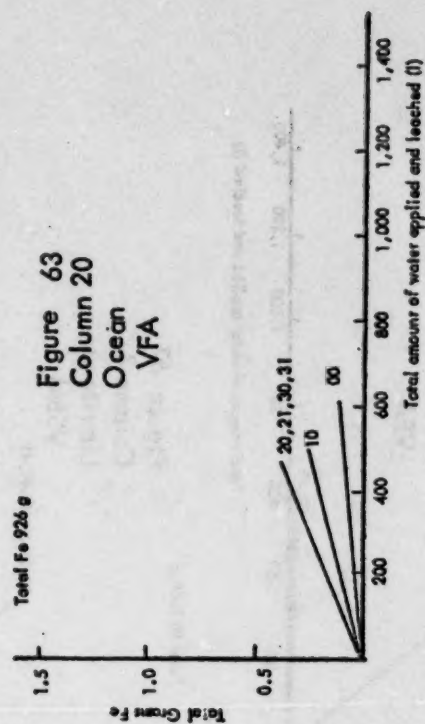
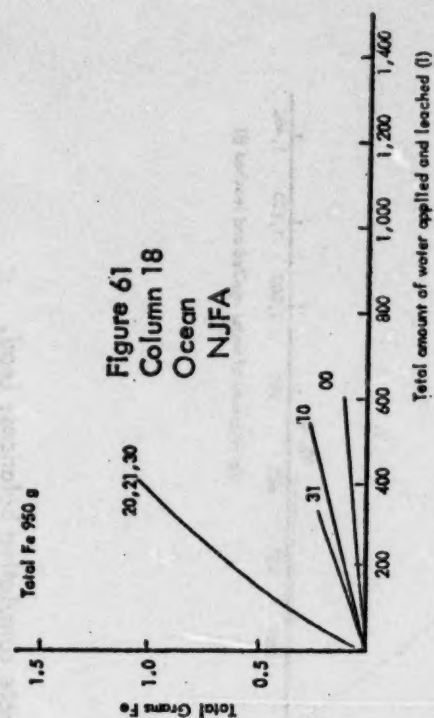
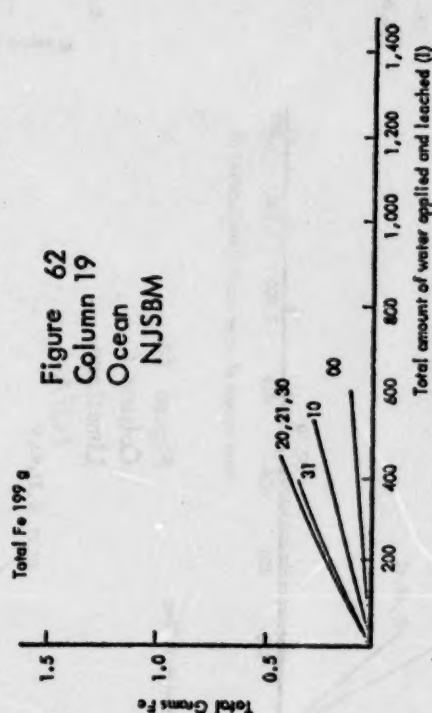
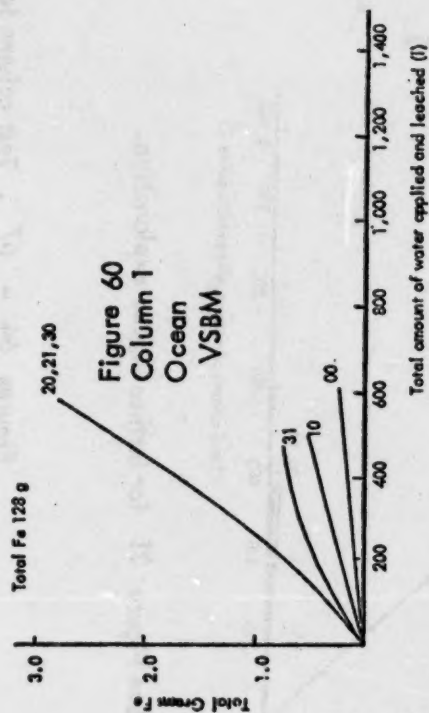
Note: See Figure 31 for further legend explanation.

Figures 52 - 55 . Test column leachate cumulative balances: Iron.



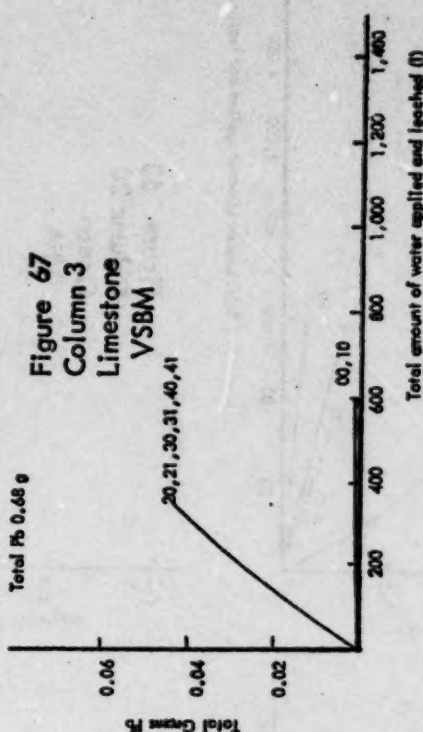
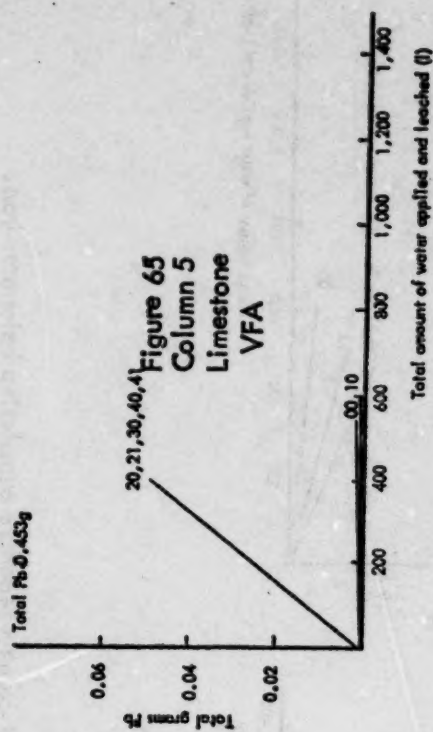
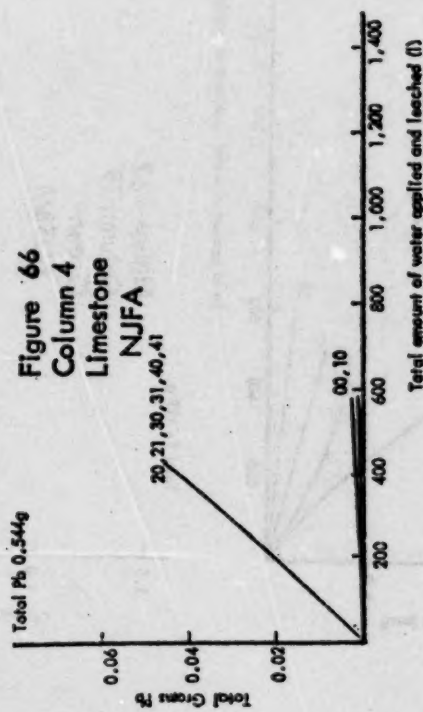
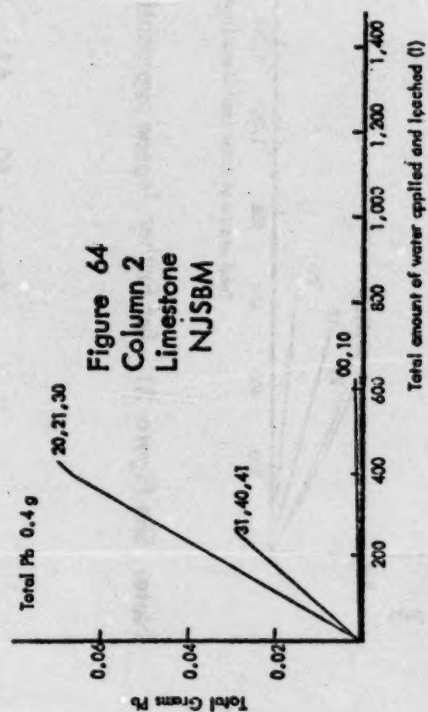
Note: See Figure 31 for further legend explanation.

Figures 56 - 59 . Test column leachate cumulative balances: Iron.



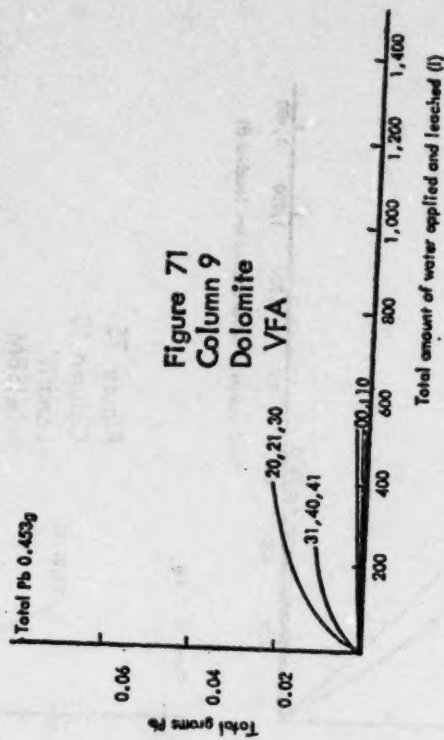
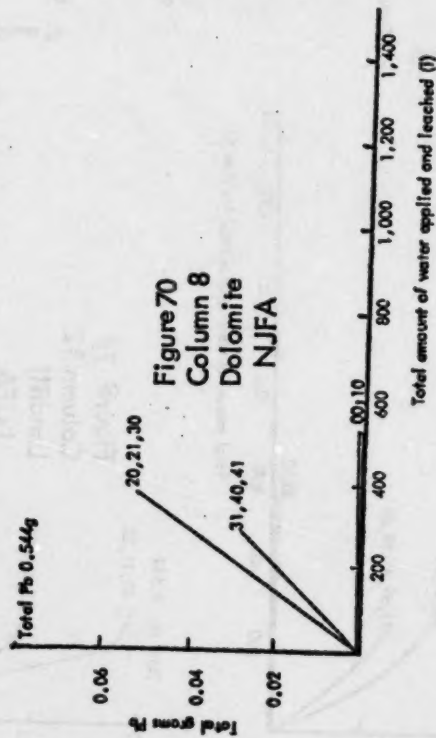
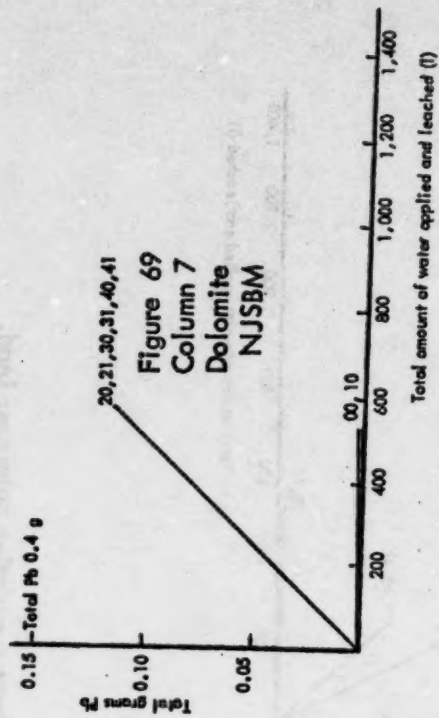
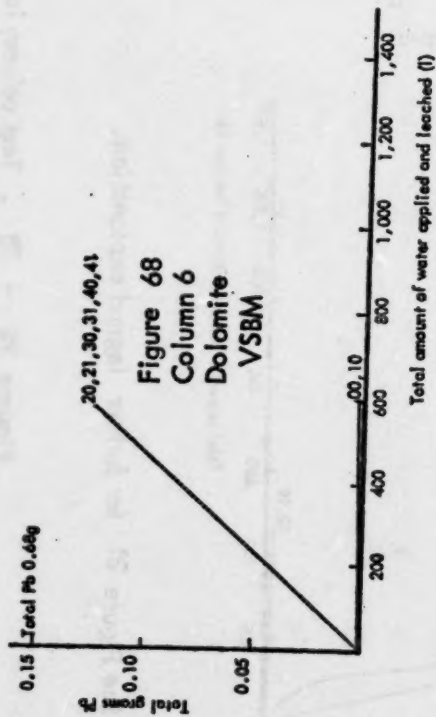
Note: See Figure 31 for further legend explanation.

Figures 60 - 63 . Test column leachate cumulative balances: Iron.



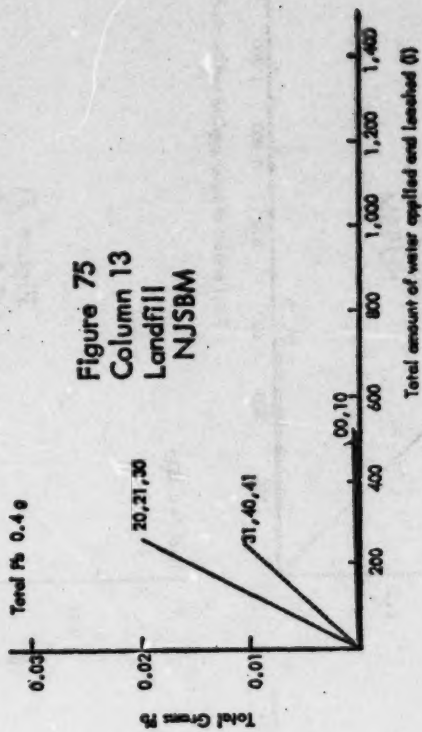
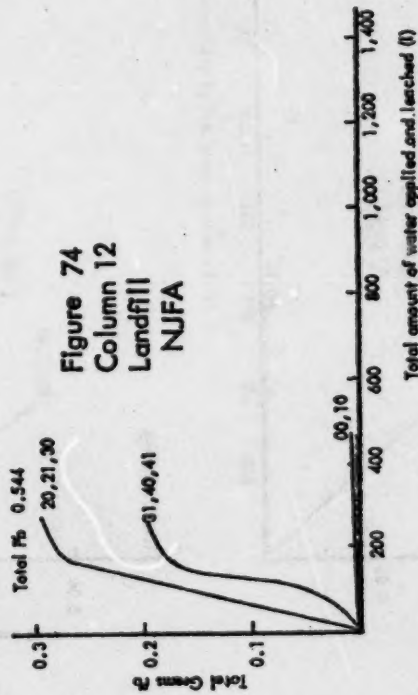
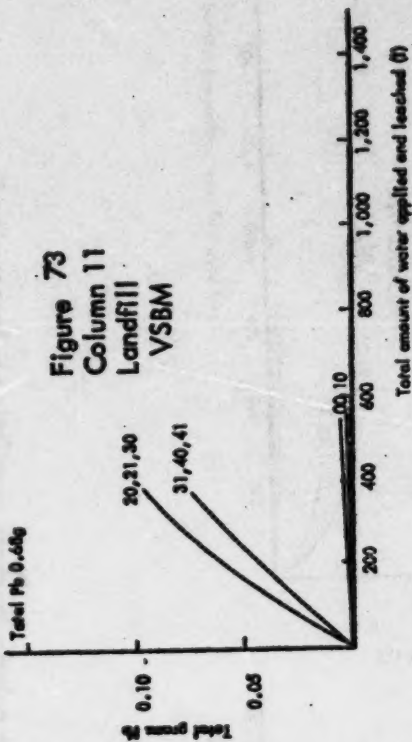
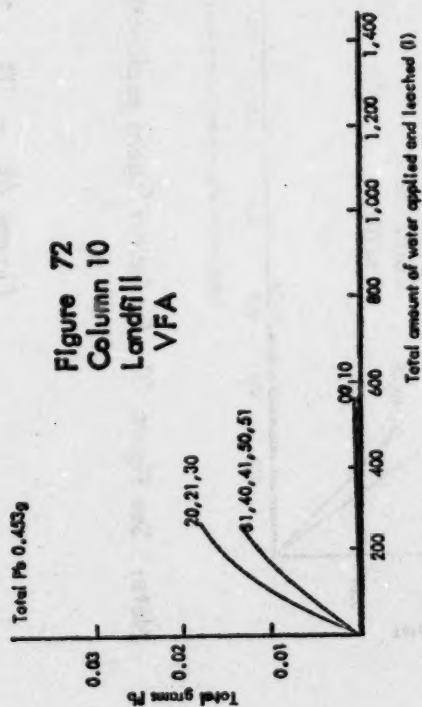
Note: See Figure 31 for further legend explanation.

Figures 64 - 67 . Test column leachate cumulative balances: Lead.



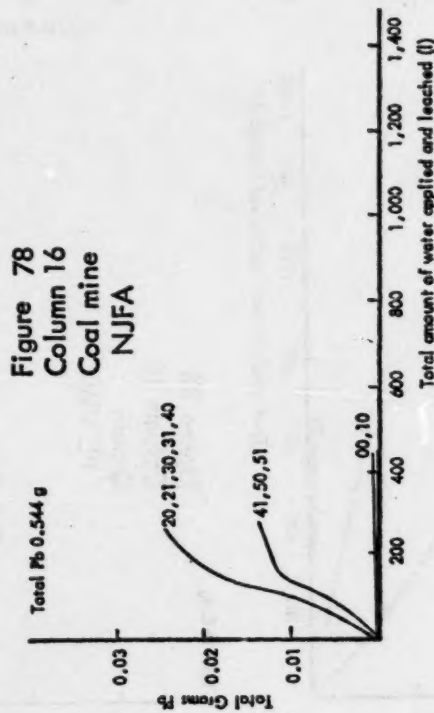
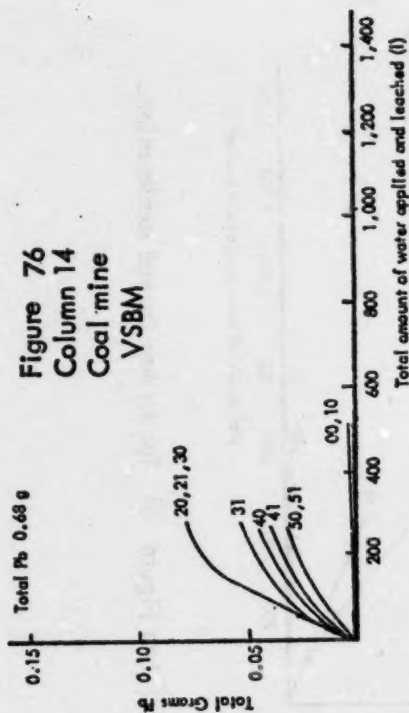
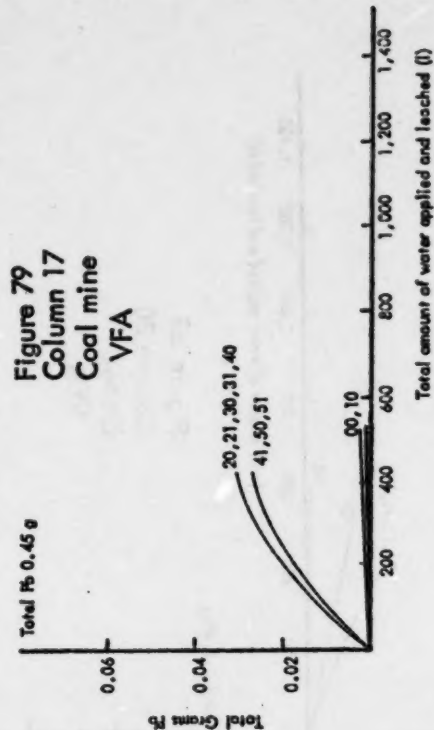
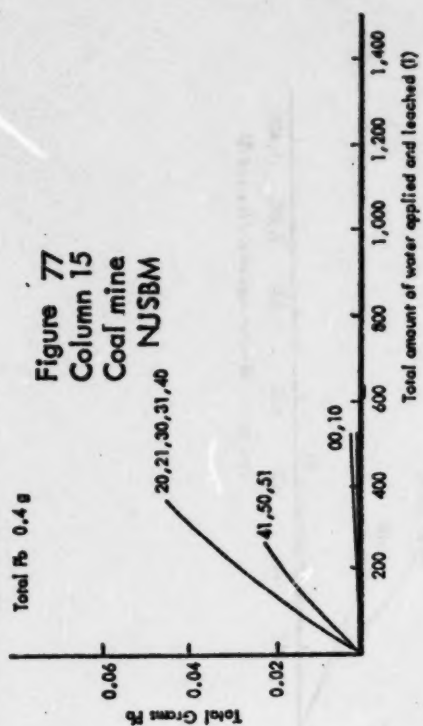
Note: See Figure 31 for further legend explanation.

Figures 68 - 71 . Test column leachate cumulative balances: Lead.



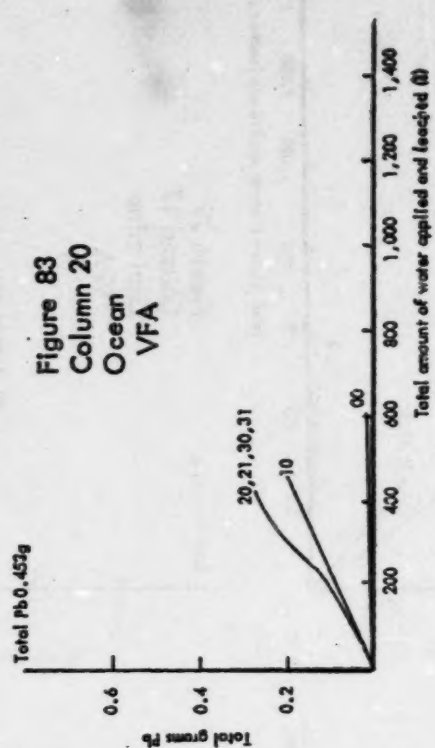
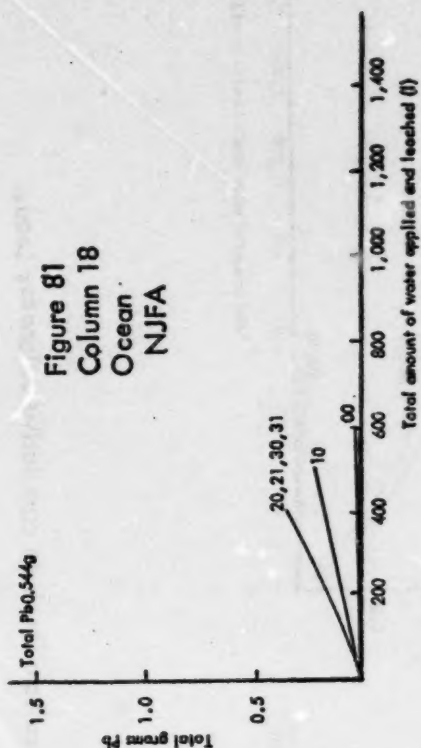
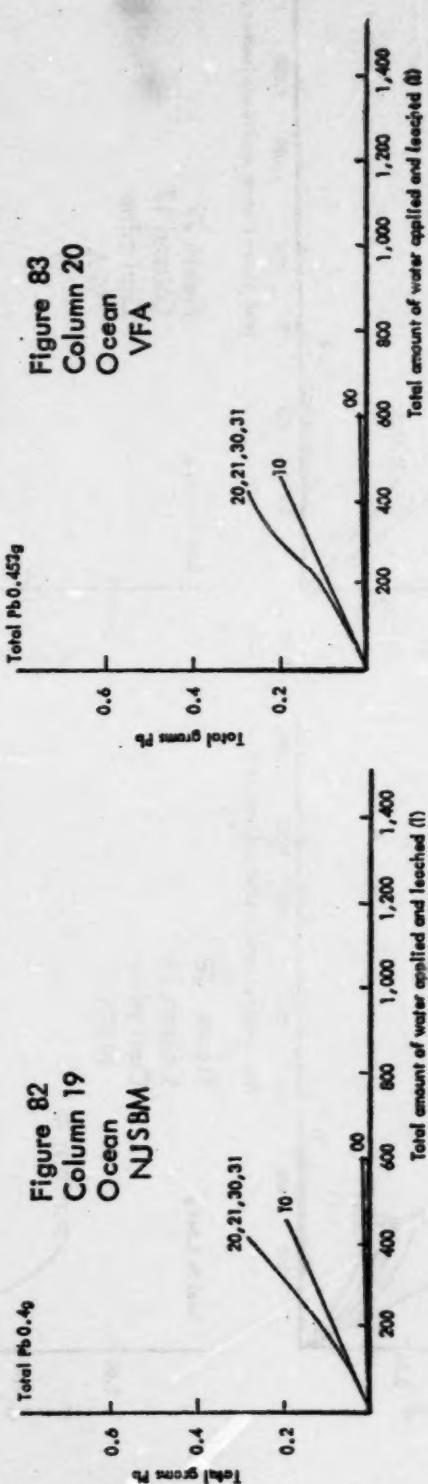
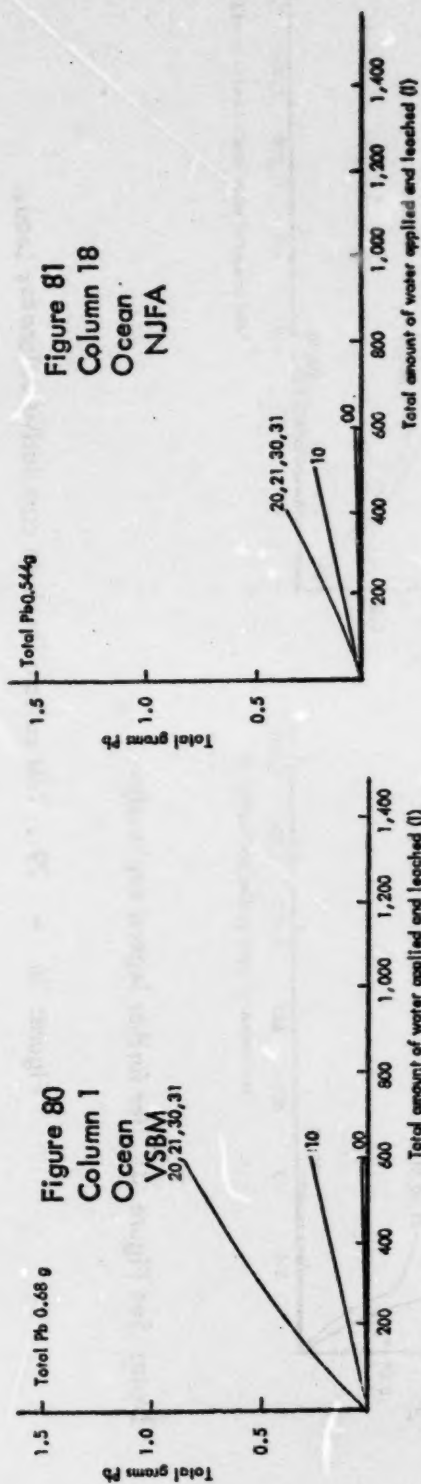
Note: See Figure 31 for further legend explanation.

Figures 72 - 75 . Test column leachate cumulative balances: Lead.



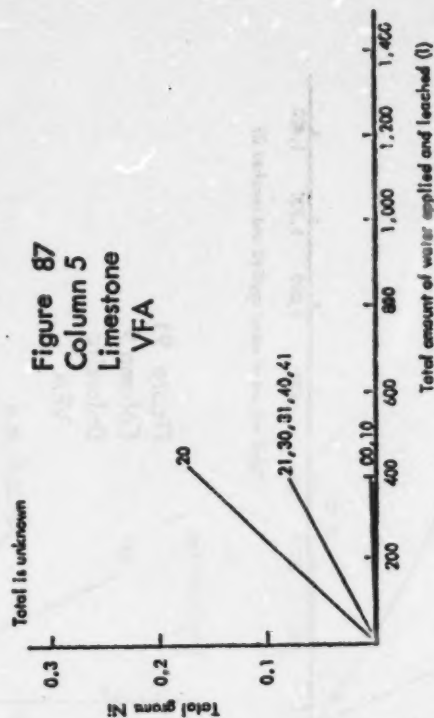
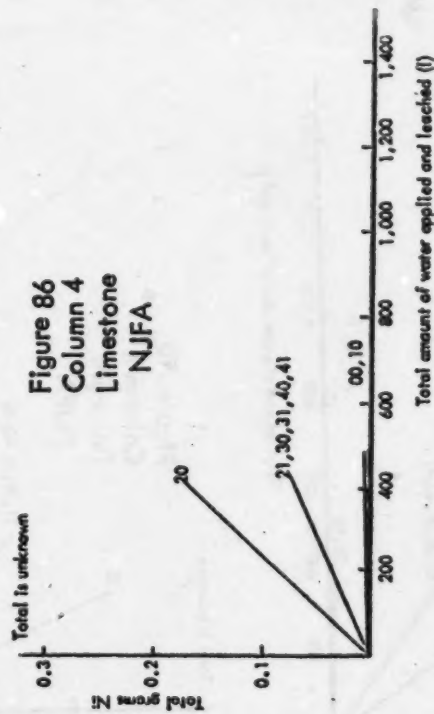
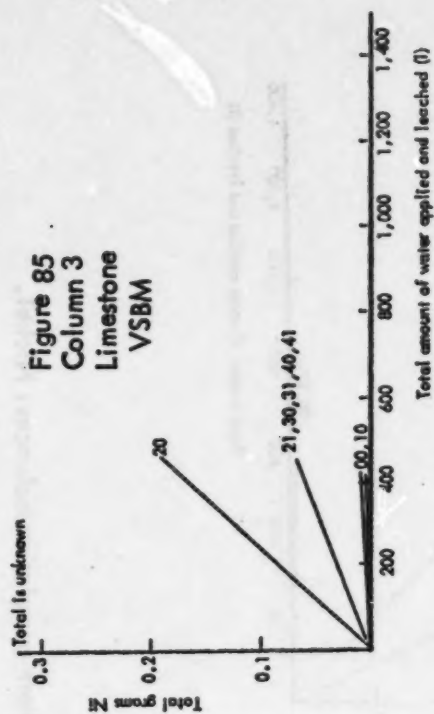
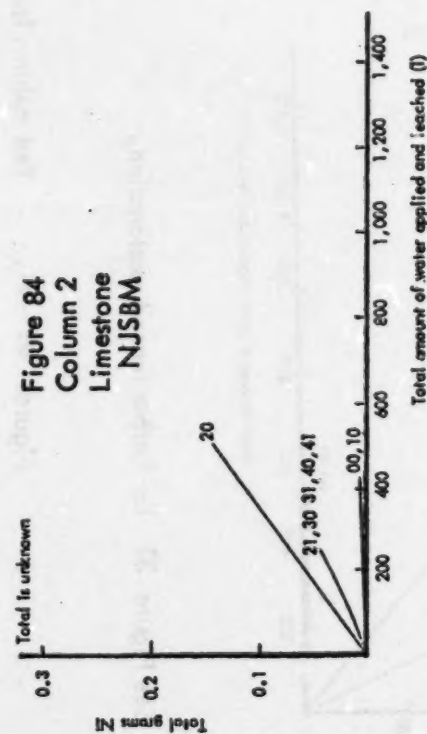
Note: See Figure 31 for further legend explanation.

Figures 76 - 79 . Test column leachate cumulative balances, Lead.



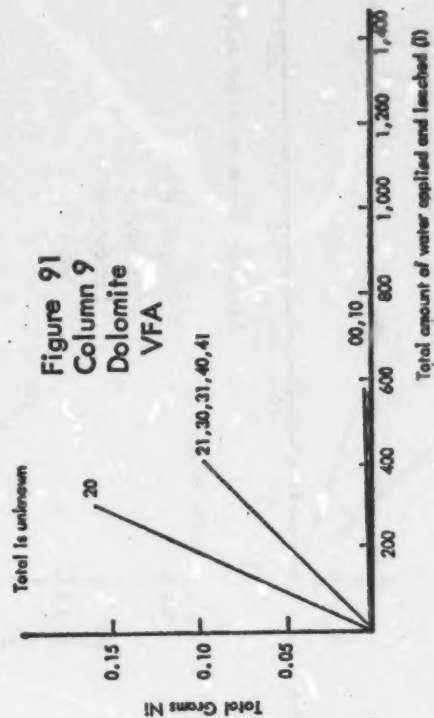
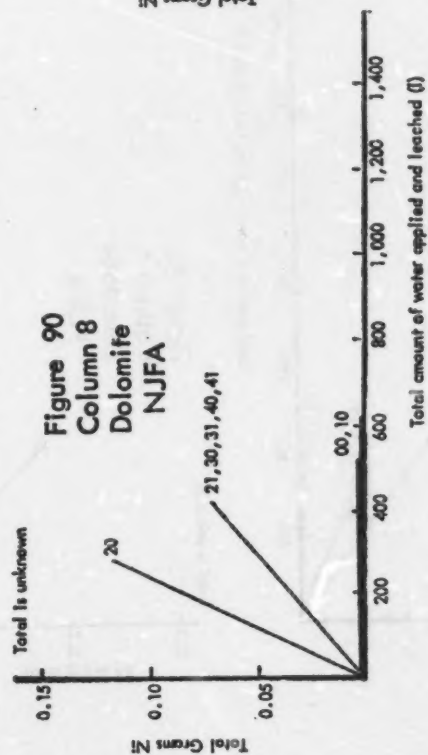
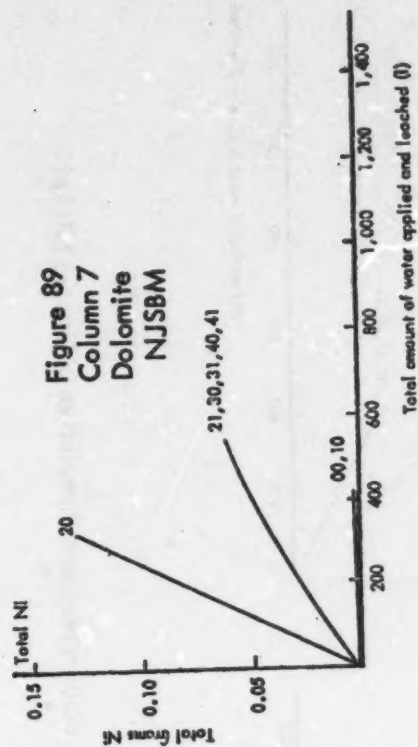
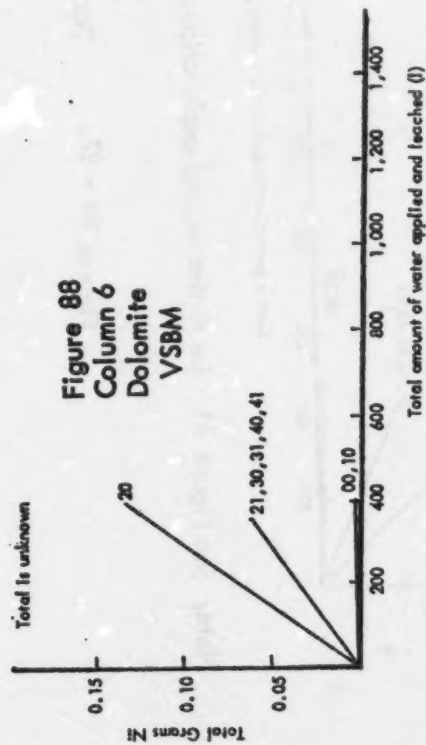
Note: See Figure 31 for further legend explanation.

Figures 80 - 83 . Test column leachate cumulative balances: Lead.



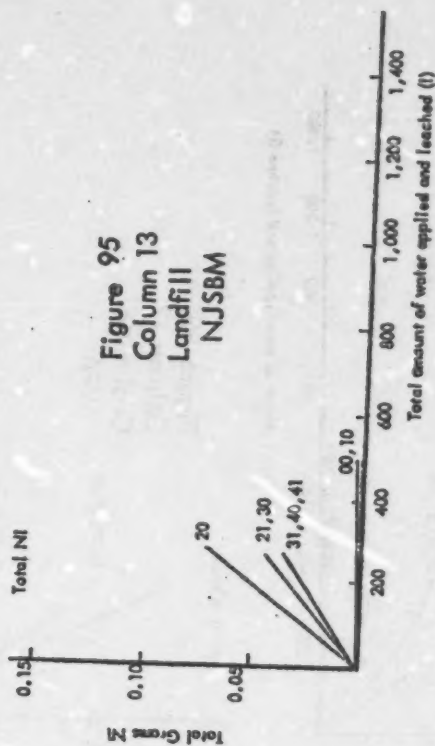
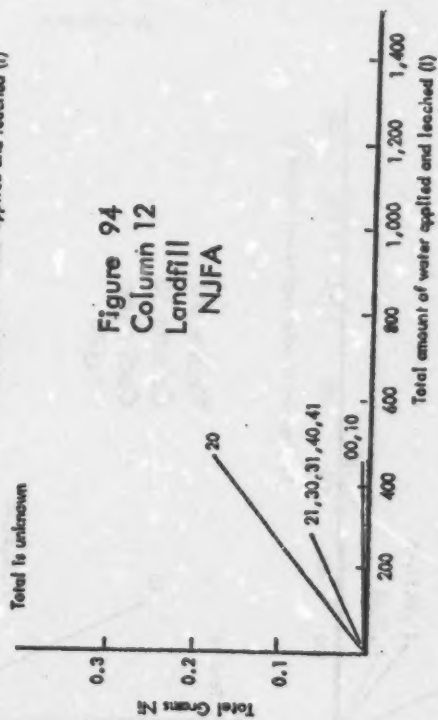
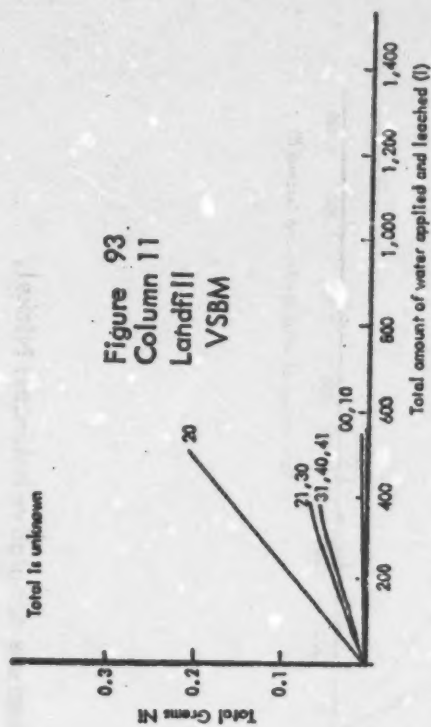
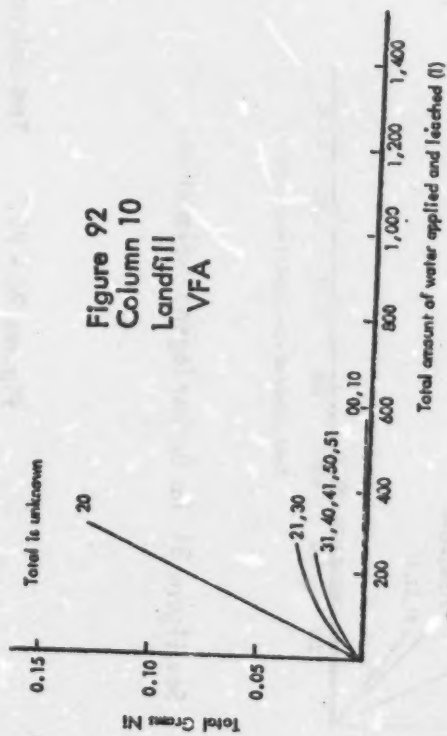
Note: See Figure 31. for further legend explanation.

Figures 84 - 87. Test column leachate cumulative balances: Nickel.



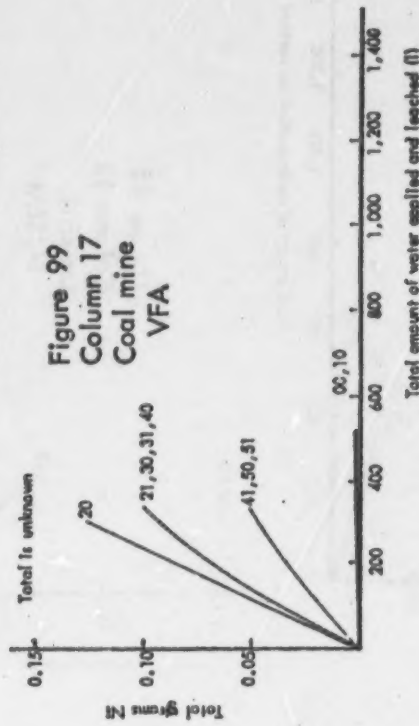
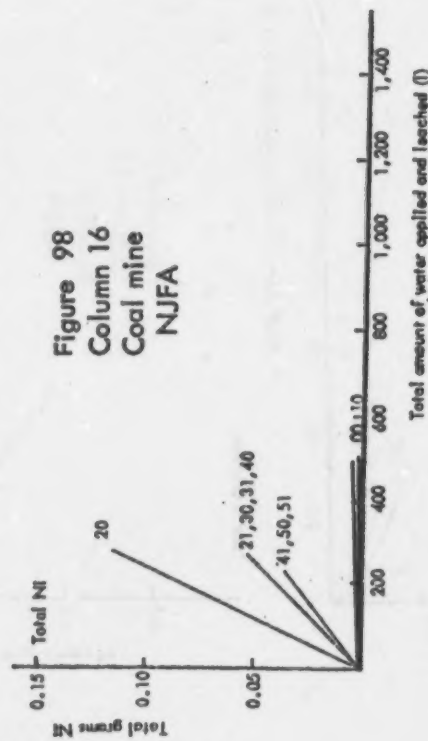
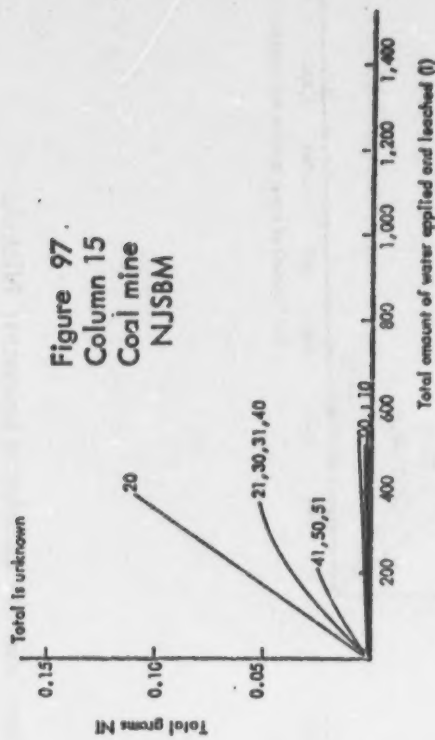
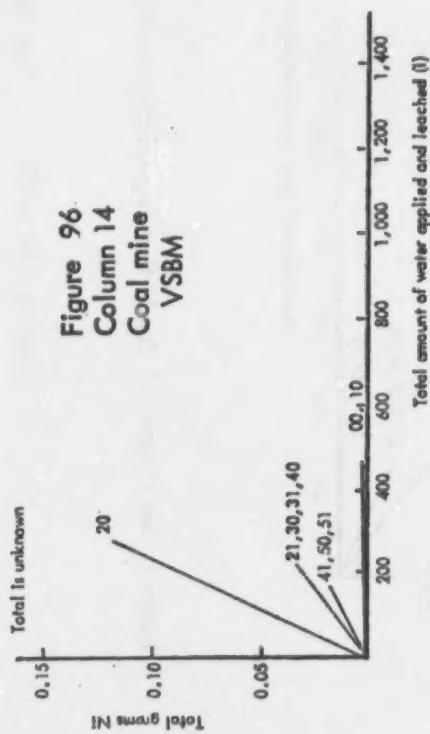
Note: See Figure 31 for further legend explanation.

Figures 88 - 91. Test column leachate cumulative balances : Nickel.



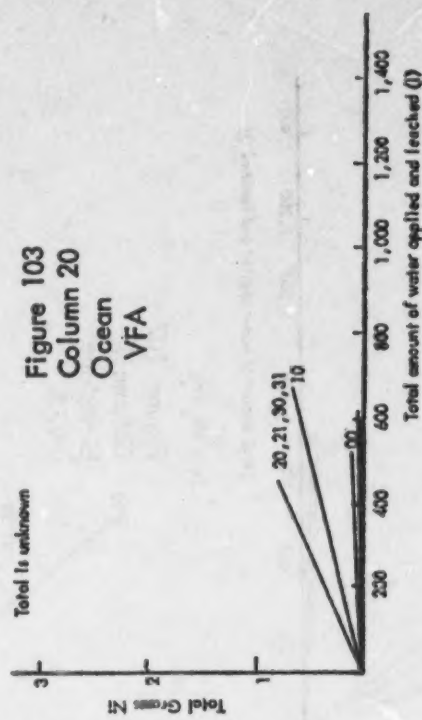
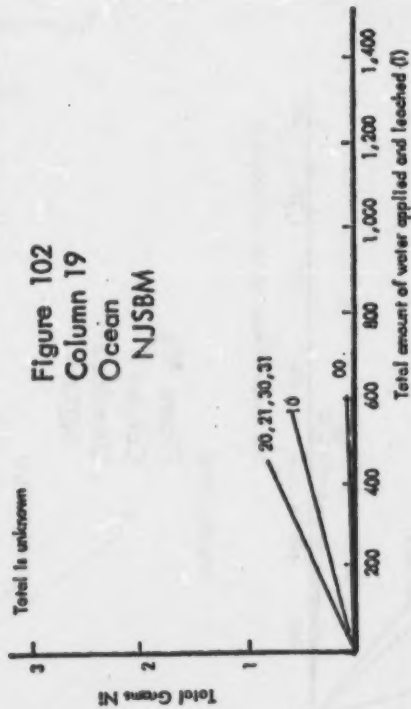
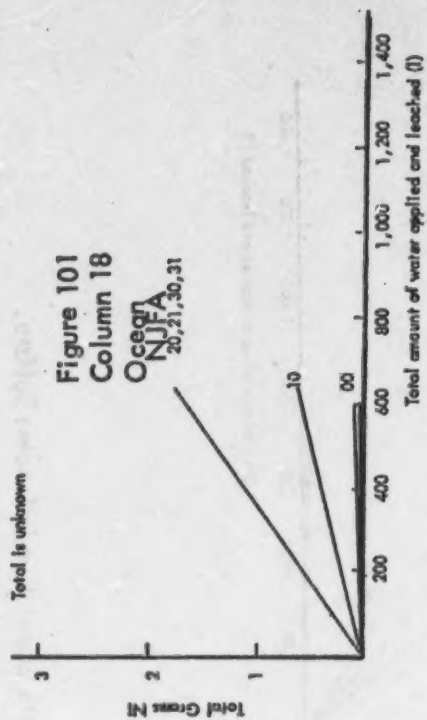
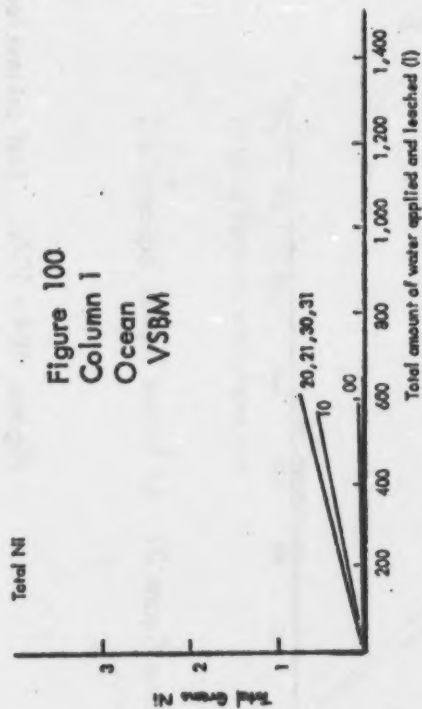
Note : See Figure 31 for further legend explanation.

Figures 92 - 95. Test column leachate cumulative balances: Nickel.



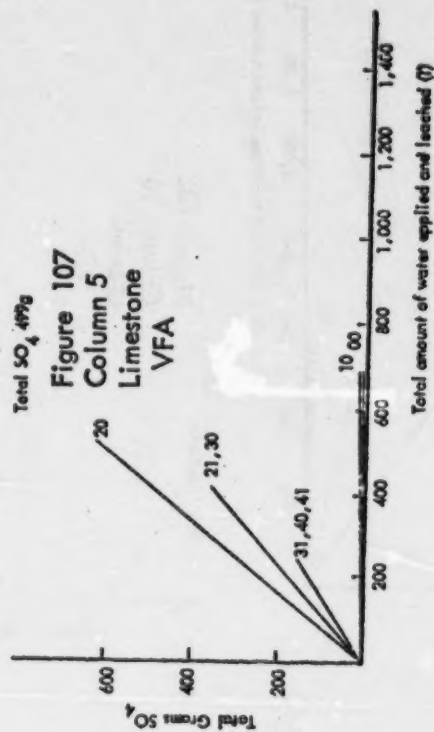
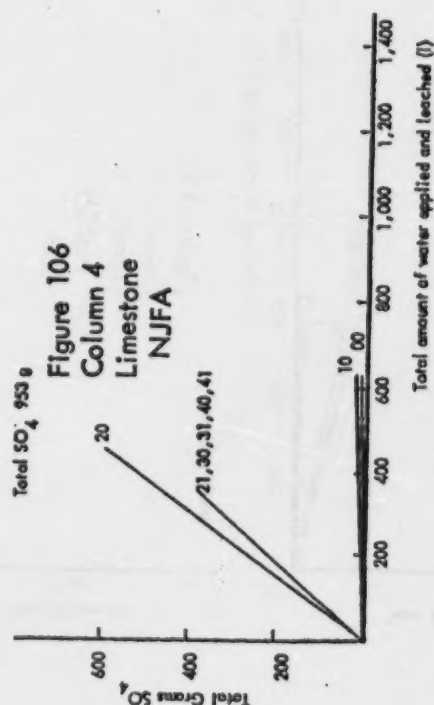
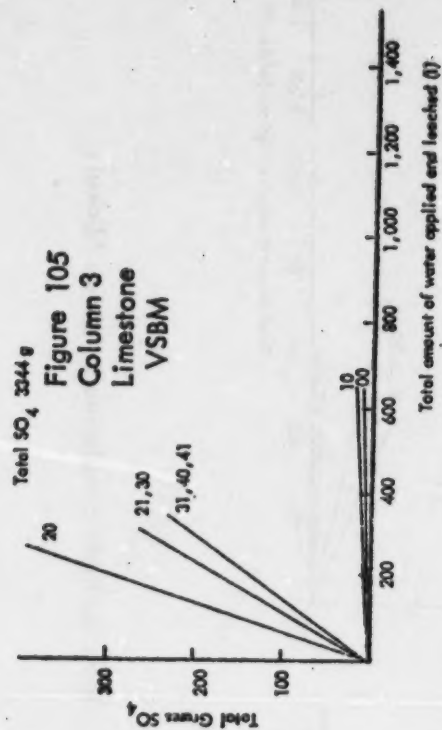
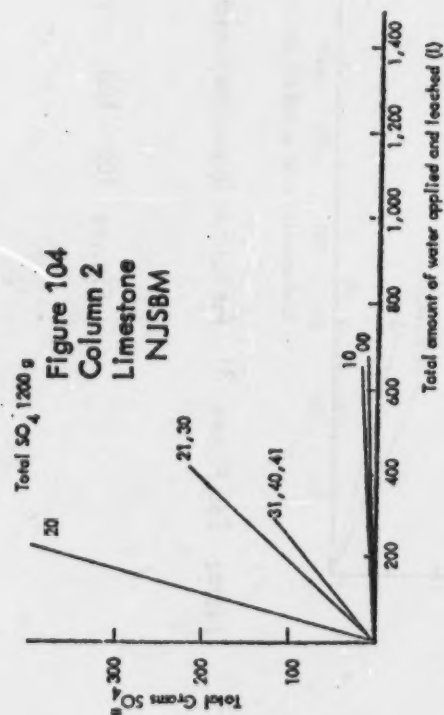
Note: See Figure 31 for further legend explanation.

Figures 96 - 99. Test column leachate cumulative balances: Nickel.



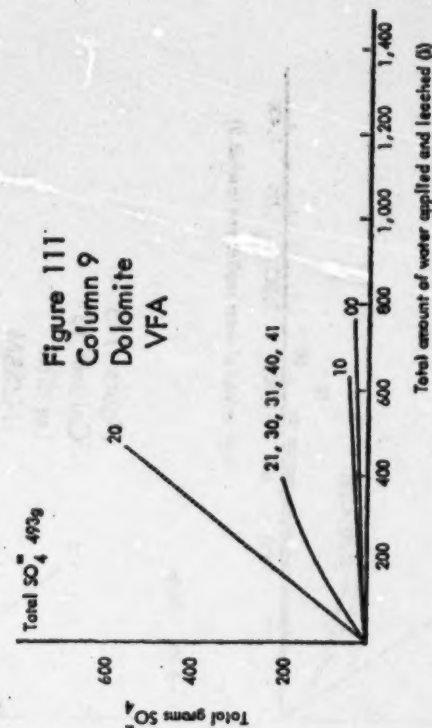
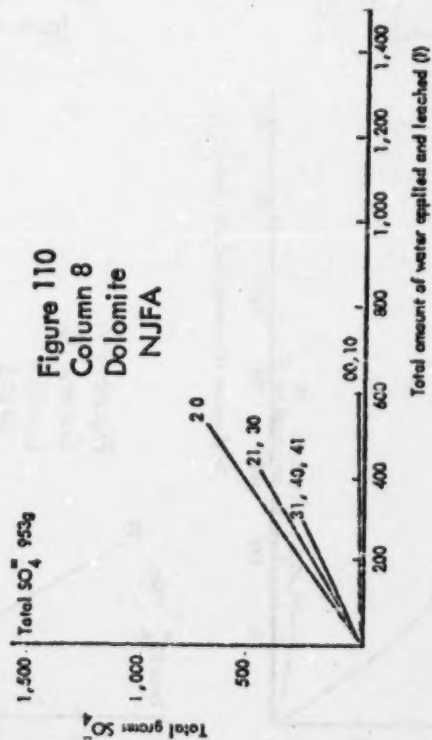
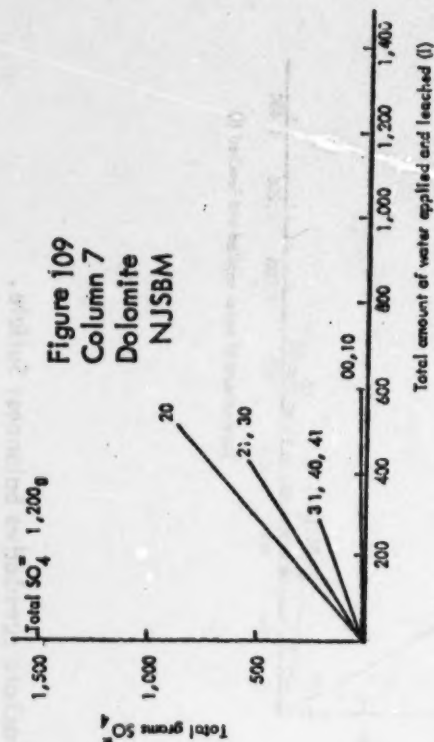
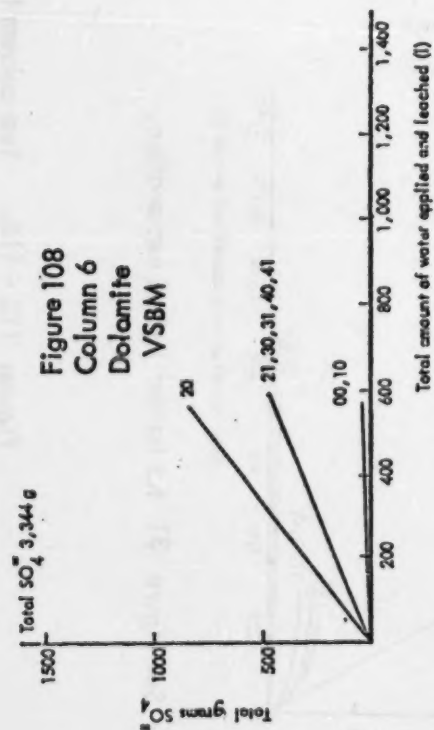
Note: See Figure 31 for further legend explanation.

Figures 100 - 103. Test column leachate cumulative balances: Nickel.



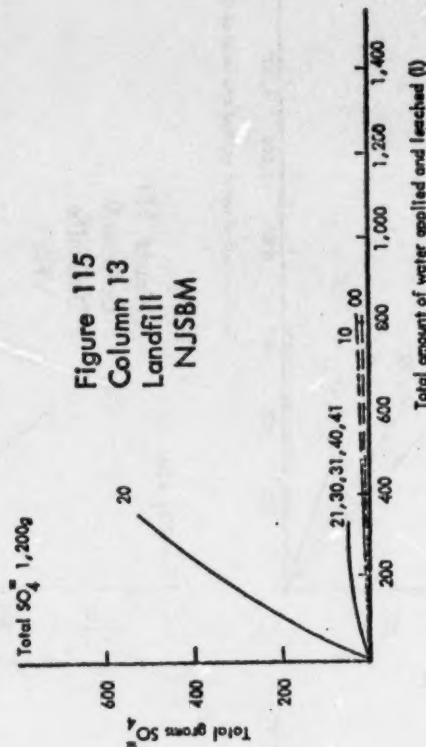
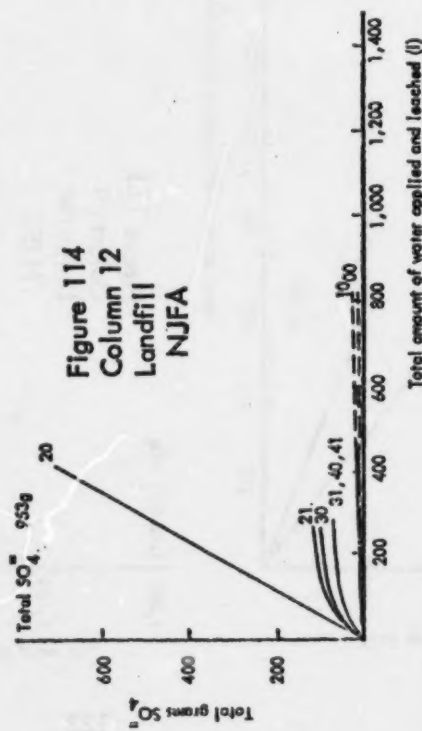
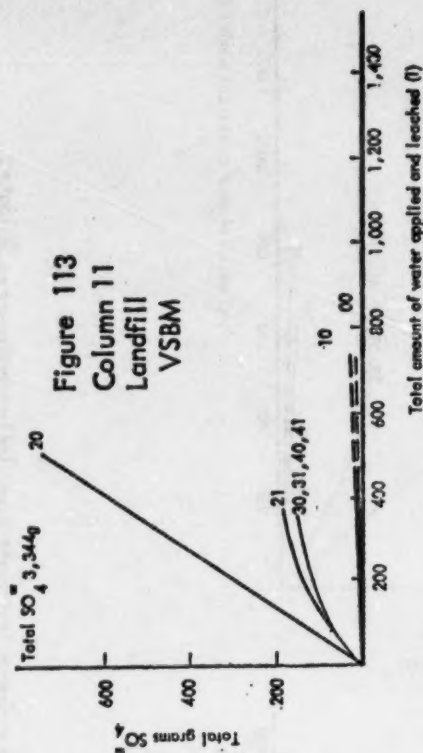
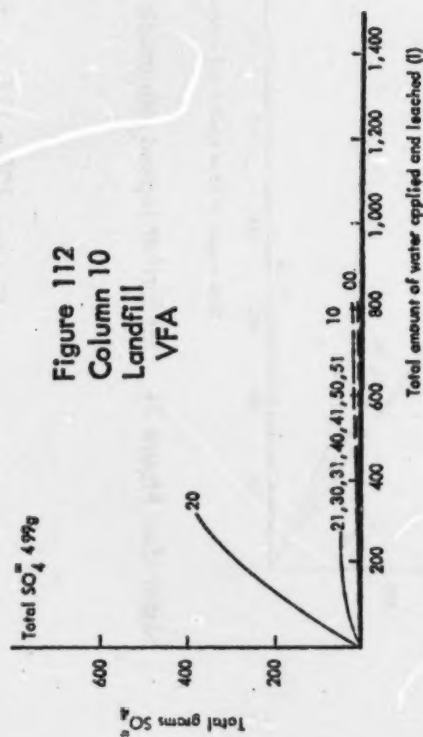
Note: See Figure 31 for further legend explanation.

Figures 104 - 107. Test column leachate cumulative balances: Sulfate.



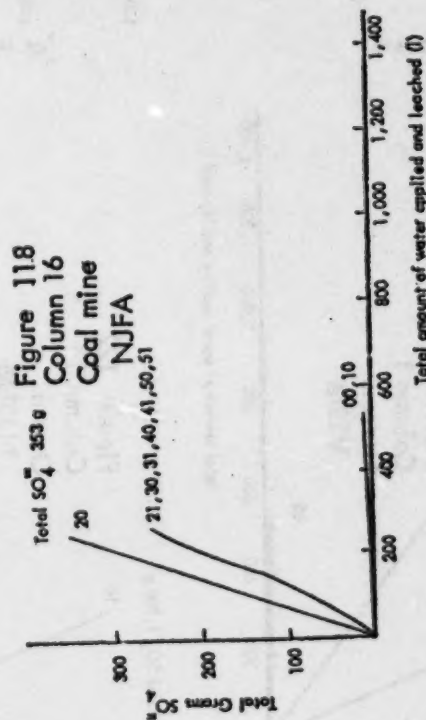
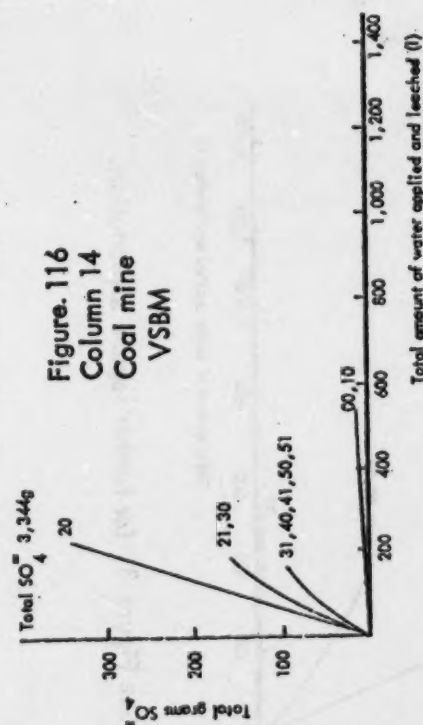
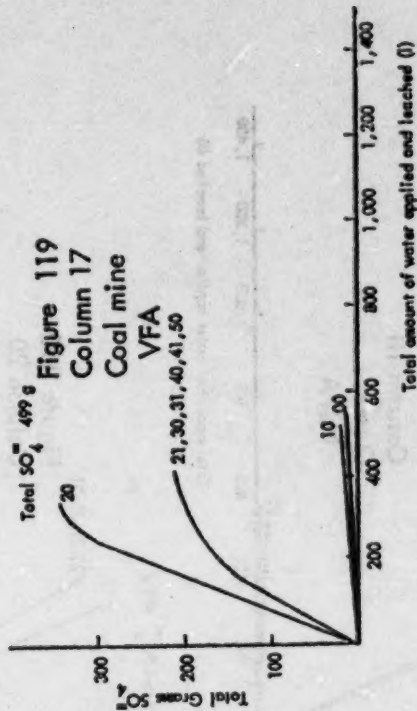
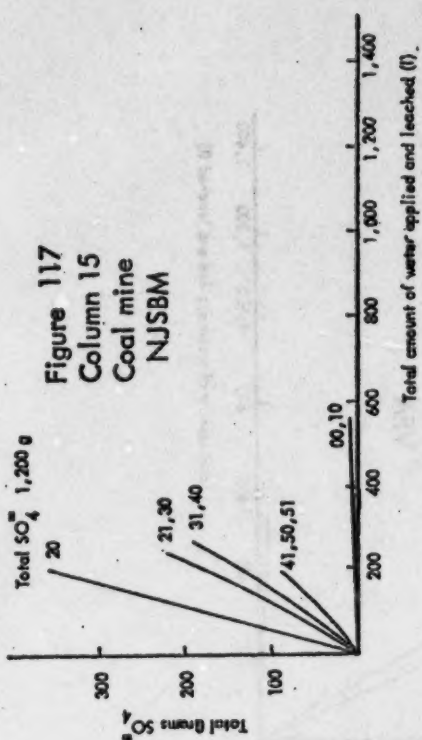
Note: See Figure 31 for further legend explanation.

Figures 108 - 111. Test column leachate cumulative balances: Sulfate.



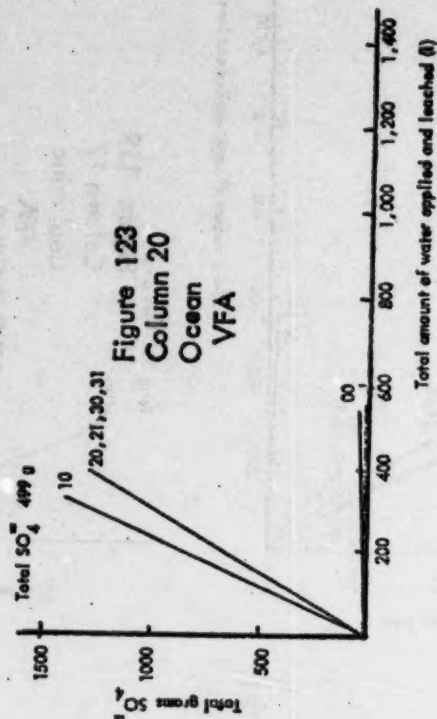
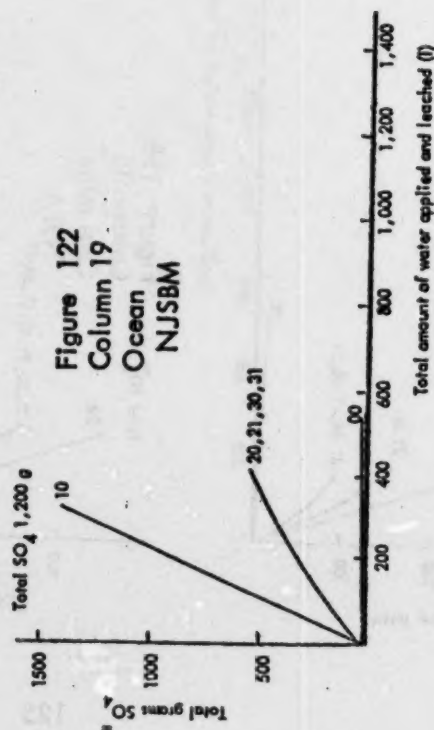
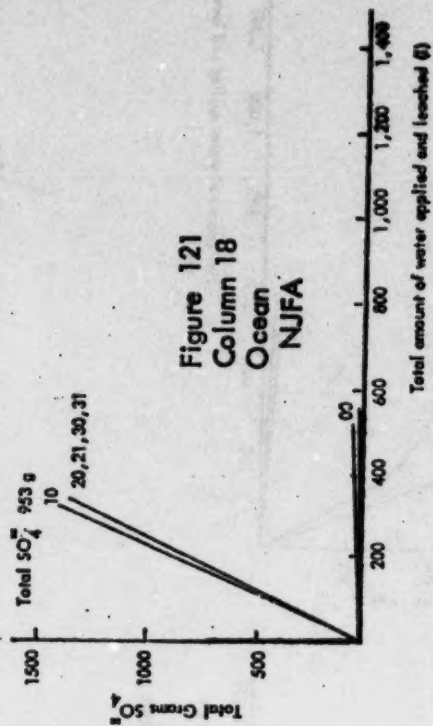
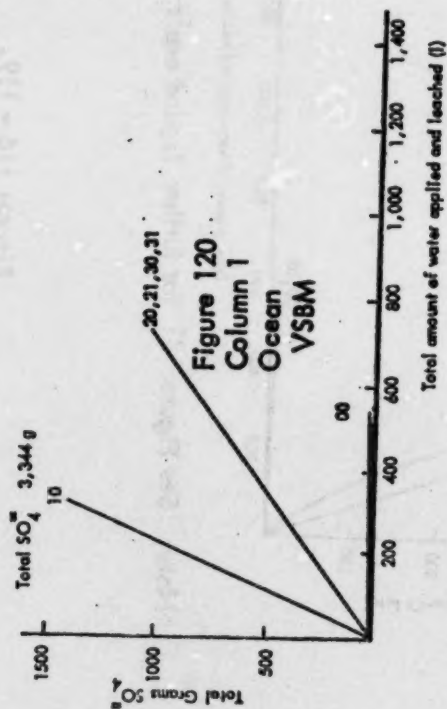
Note: See Figure 31 for further legend explanation.

Figures 112 - 115. Test column leachate cumulative balances: Sulfate.



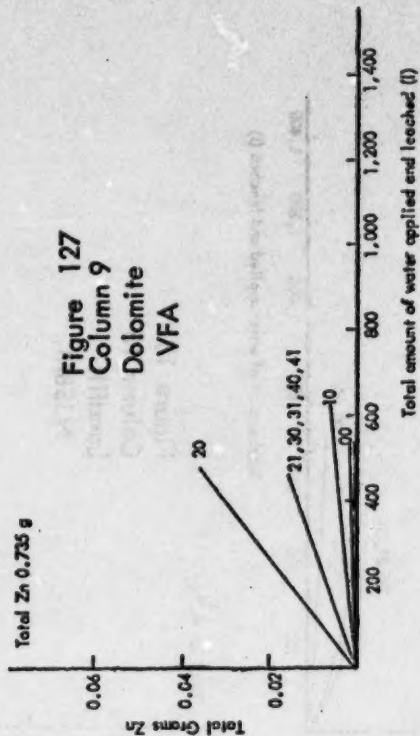
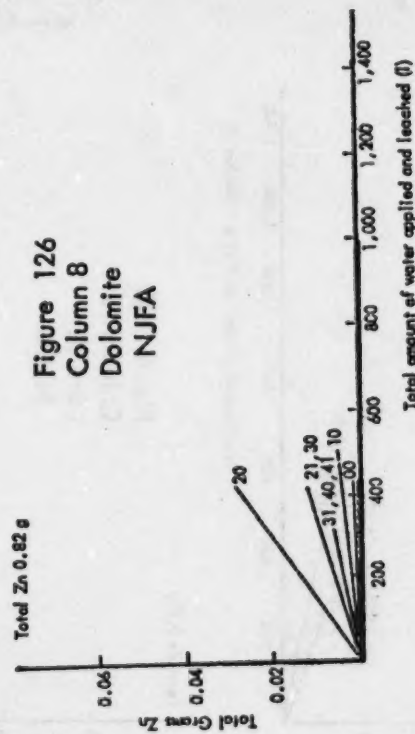
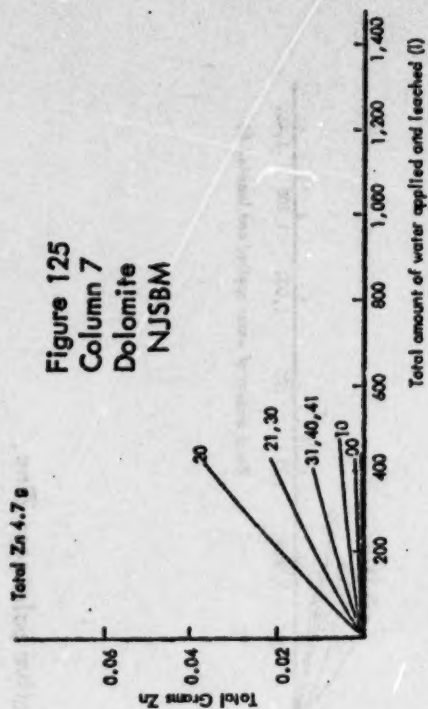
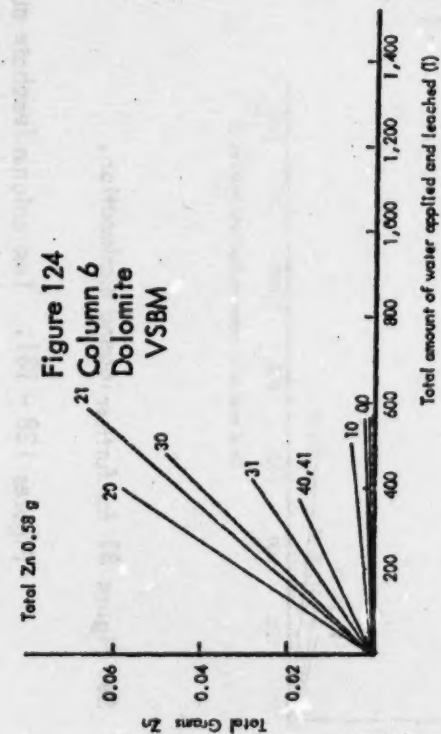
Note: See Figure 31 for further legend explanation.

Figures 116 - 119. Test column leachate cumulative balances : Sulfate.



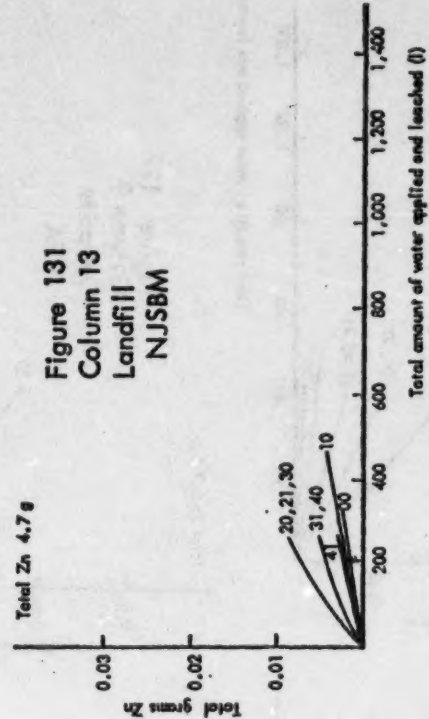
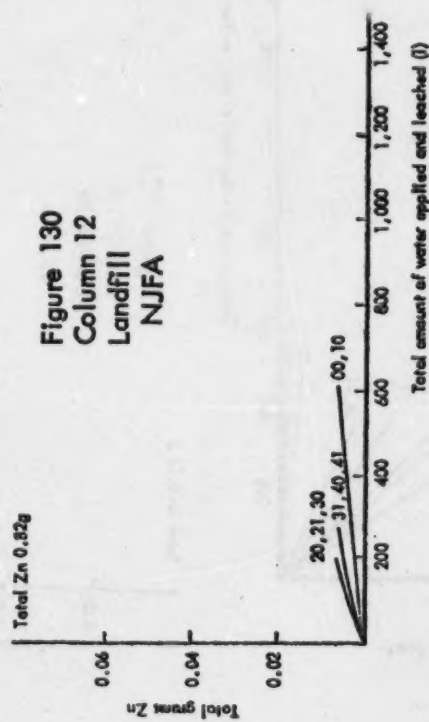
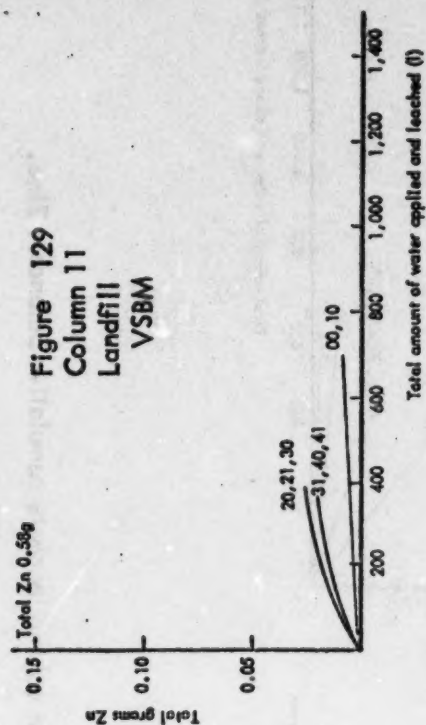
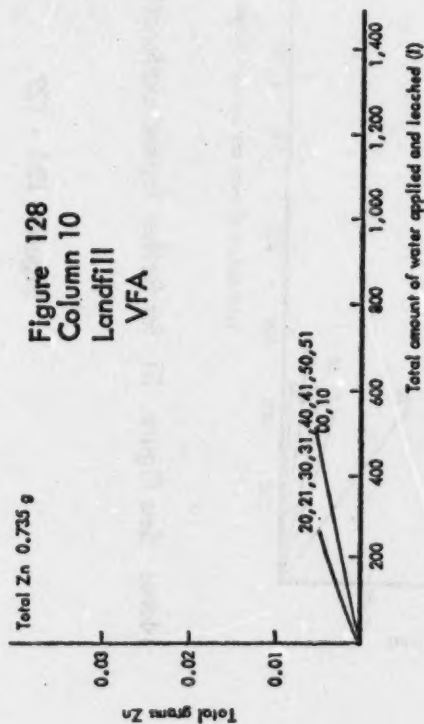
Note: See Figure 31 for further legend explanation.

Figures 120 - 123. Test column leachate cumulative balances: Sulfate.



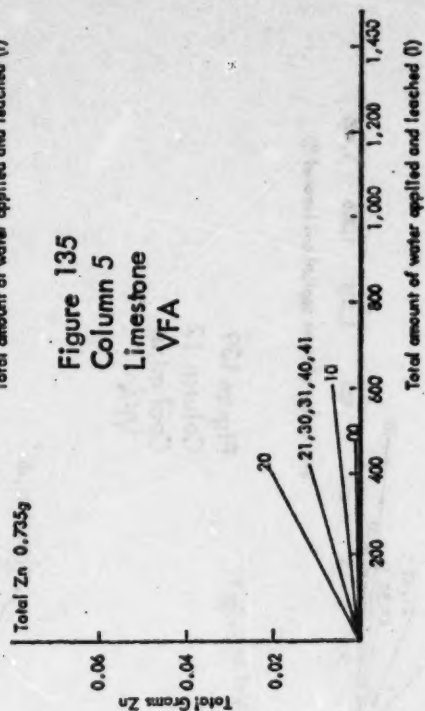
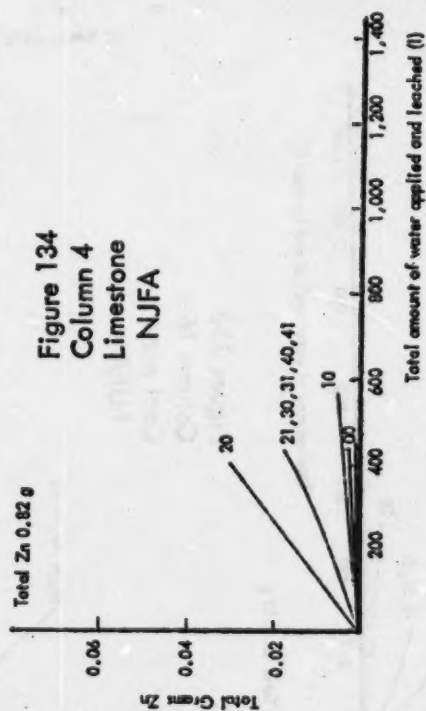
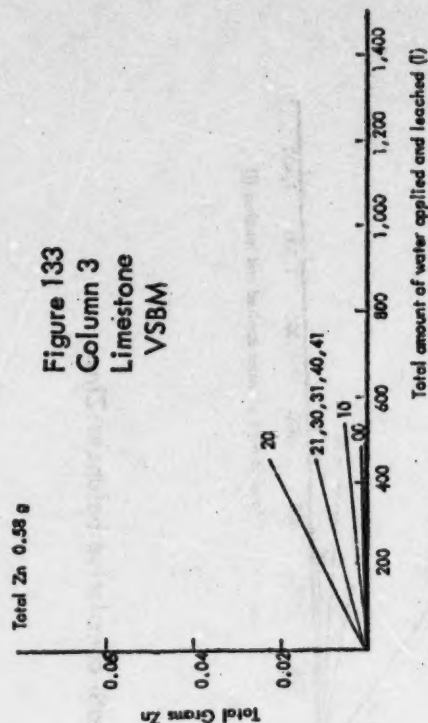
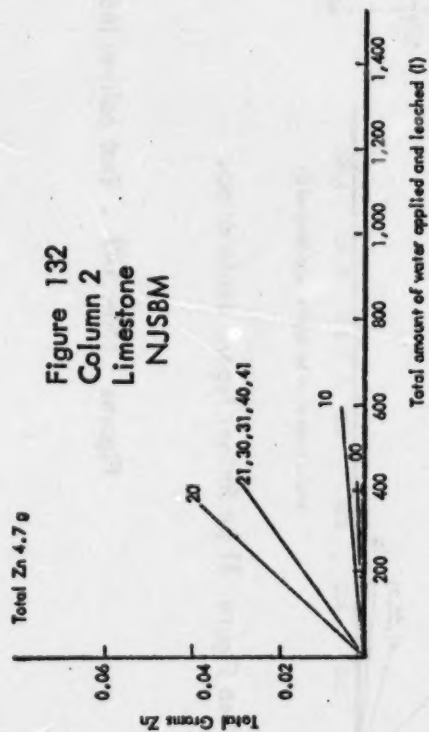
Note: See Figure 31 for further legend explanation.

Figures 124 - 127. Test column leachate cumulative balances: Zinc.



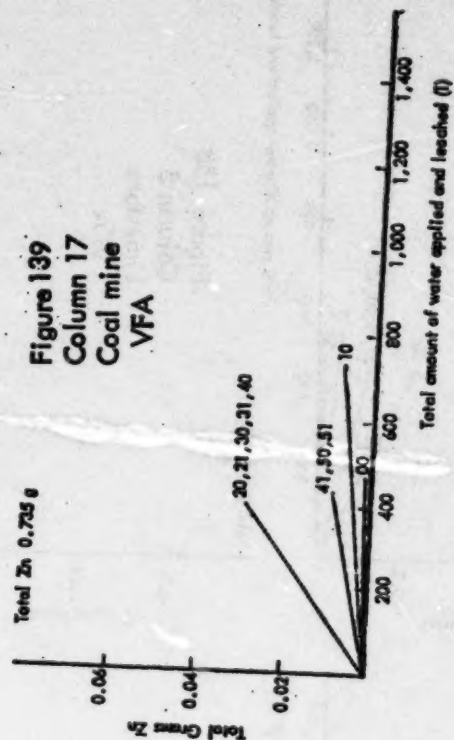
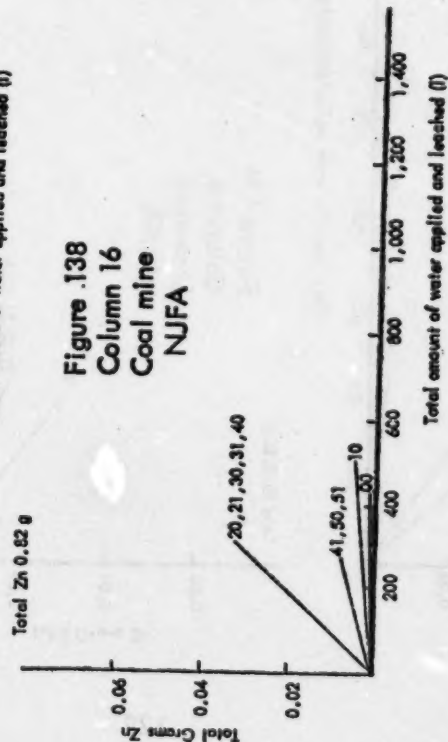
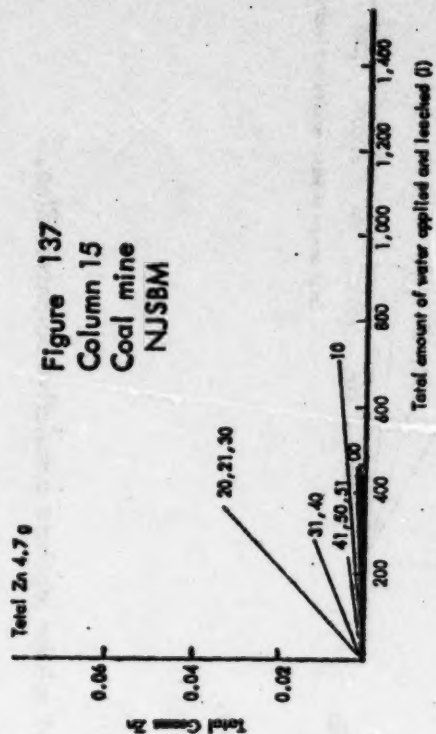
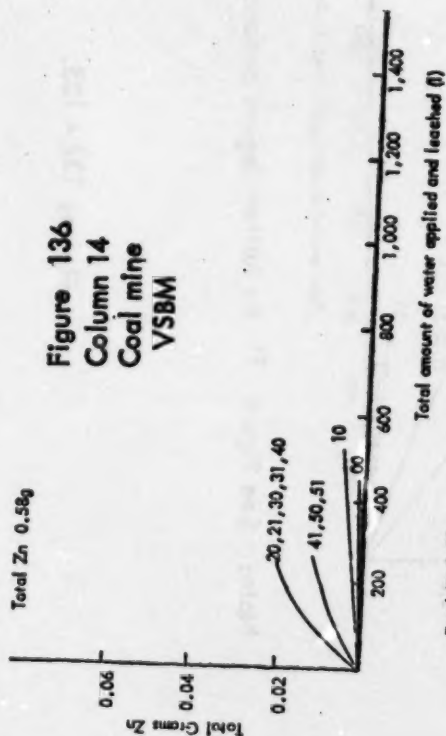
Note: See Figure 31 for further legend explanation.

Figures 128 - 131. Test column leachate cumulative balances: Zinc.



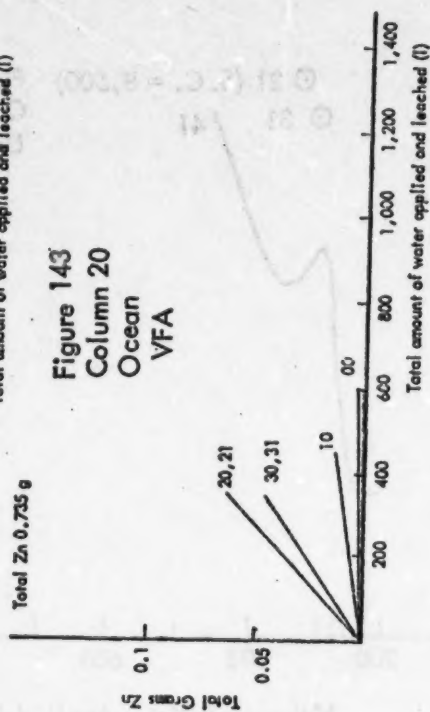
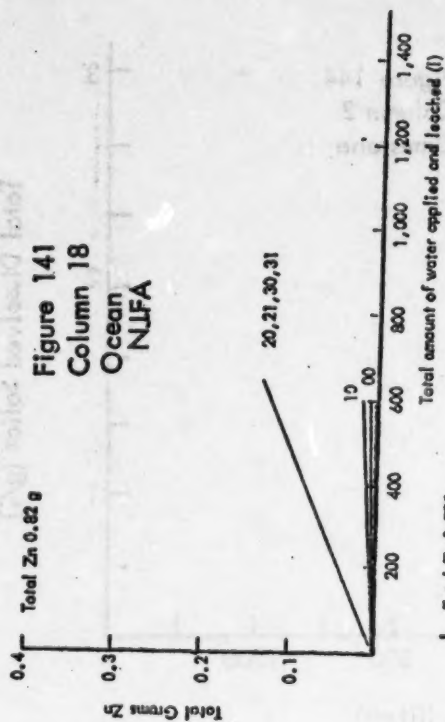
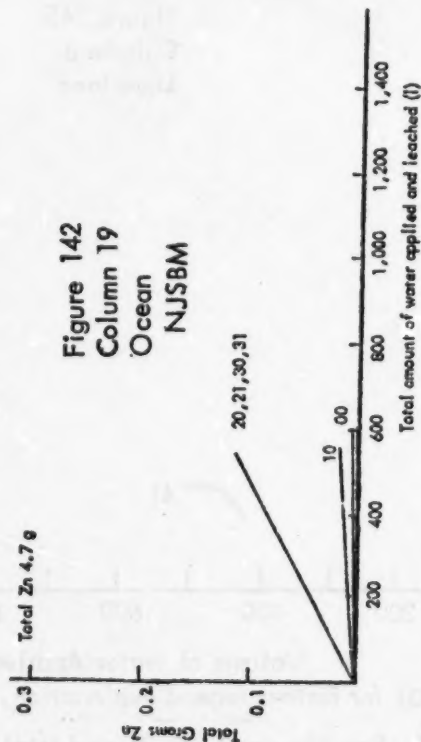
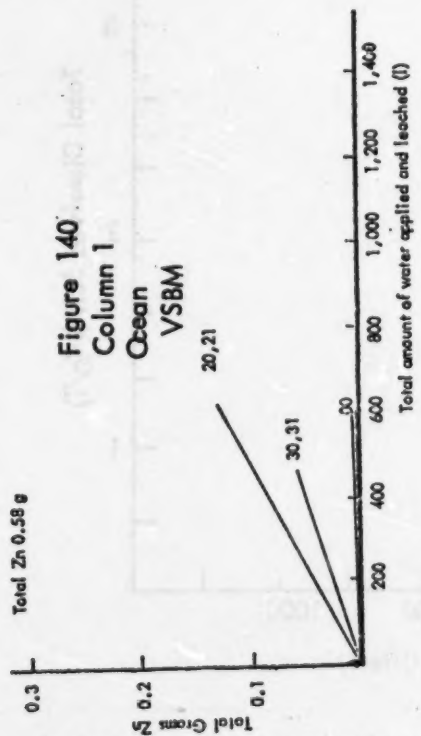
Note: See Figure 31 for further legend explanation.

Figures 132 - 135. Test column leachate cumulative balances: Zinc.



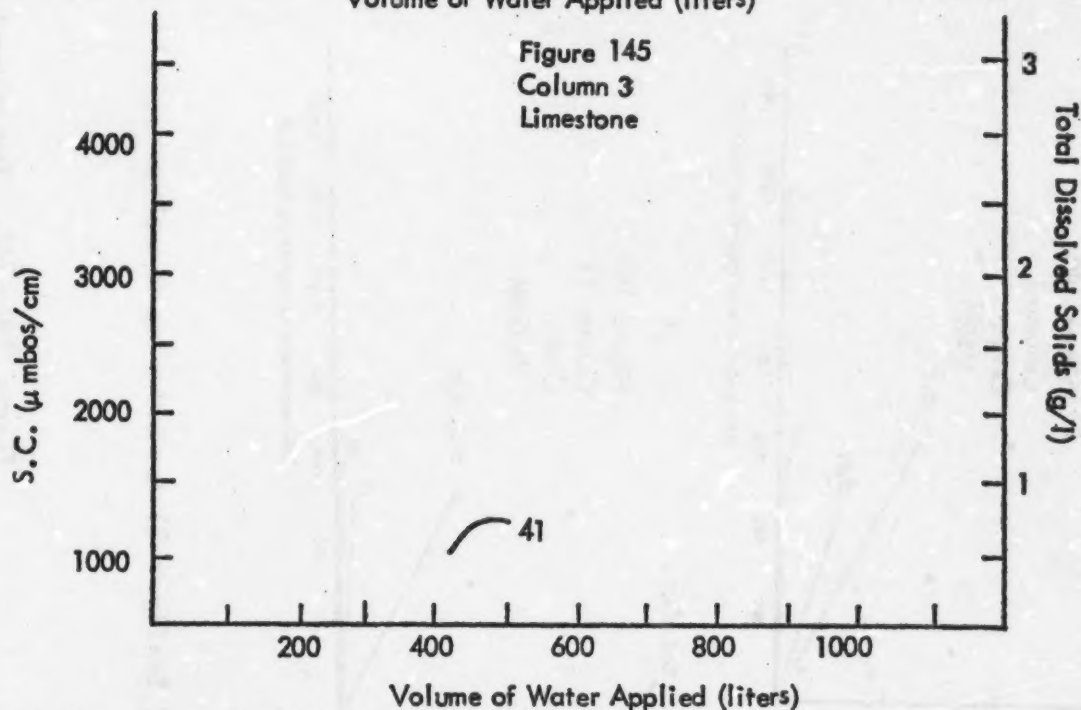
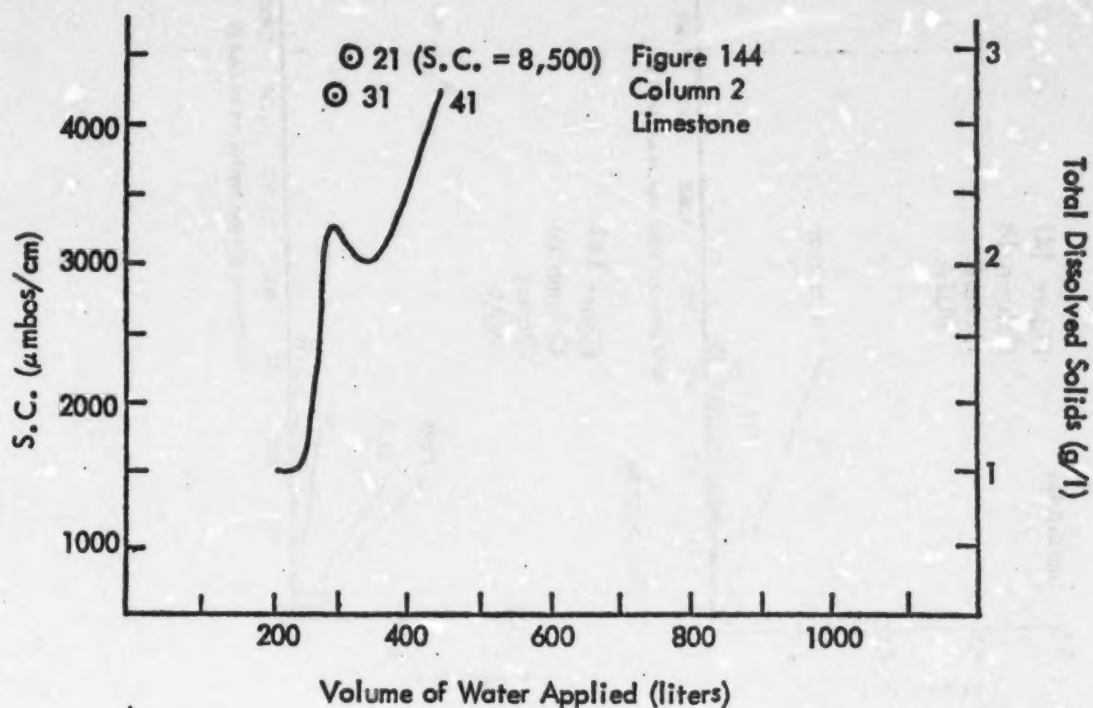
Note: See Figure 31 for further legend explanation.

Figures 136- 139 . Test column leachate cumulative balances:Zinc.



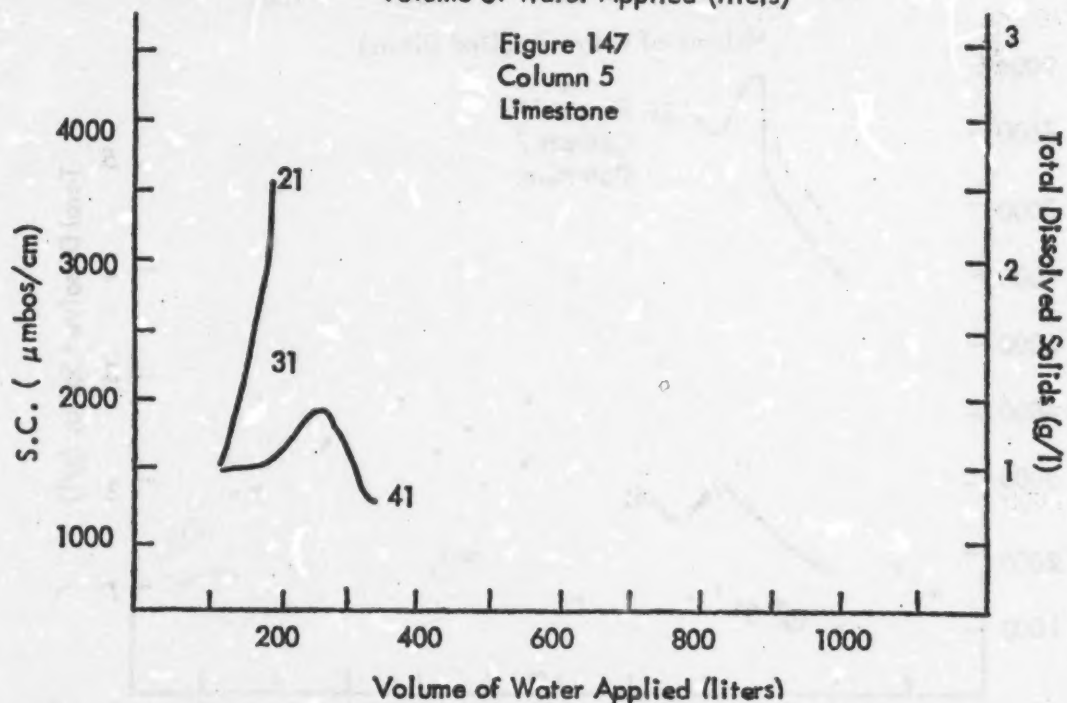
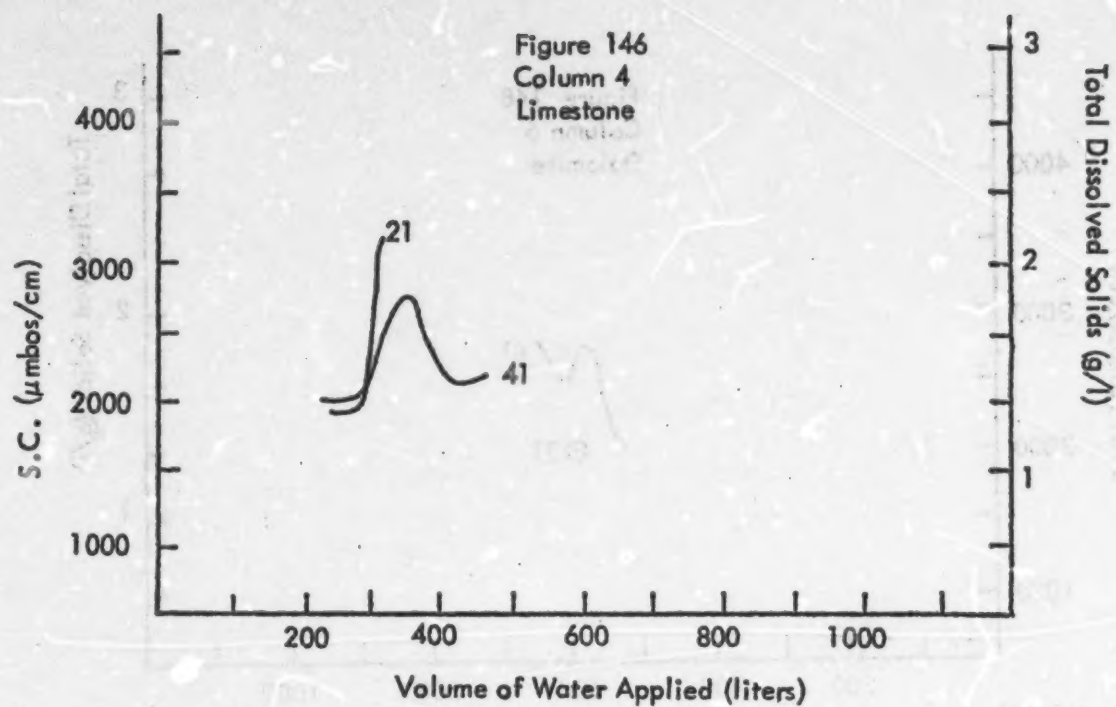
Note: See Figure 31 for further legend explanation.

Figures 140 - 143. Test column leachate cumulative balances: Zinc.



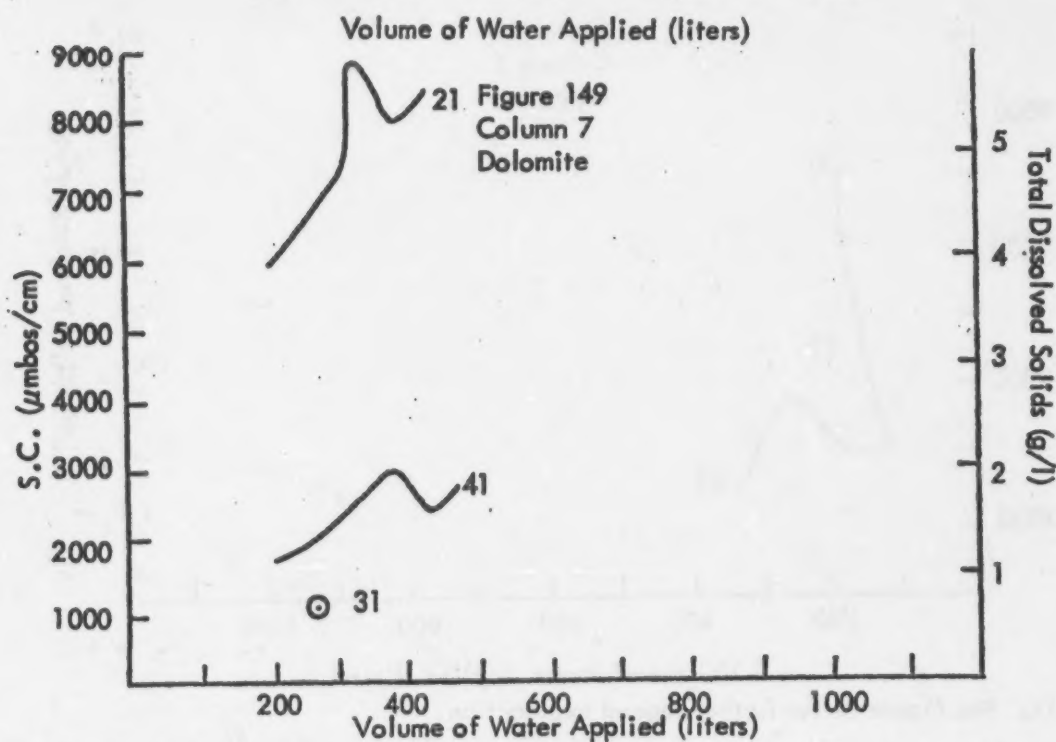
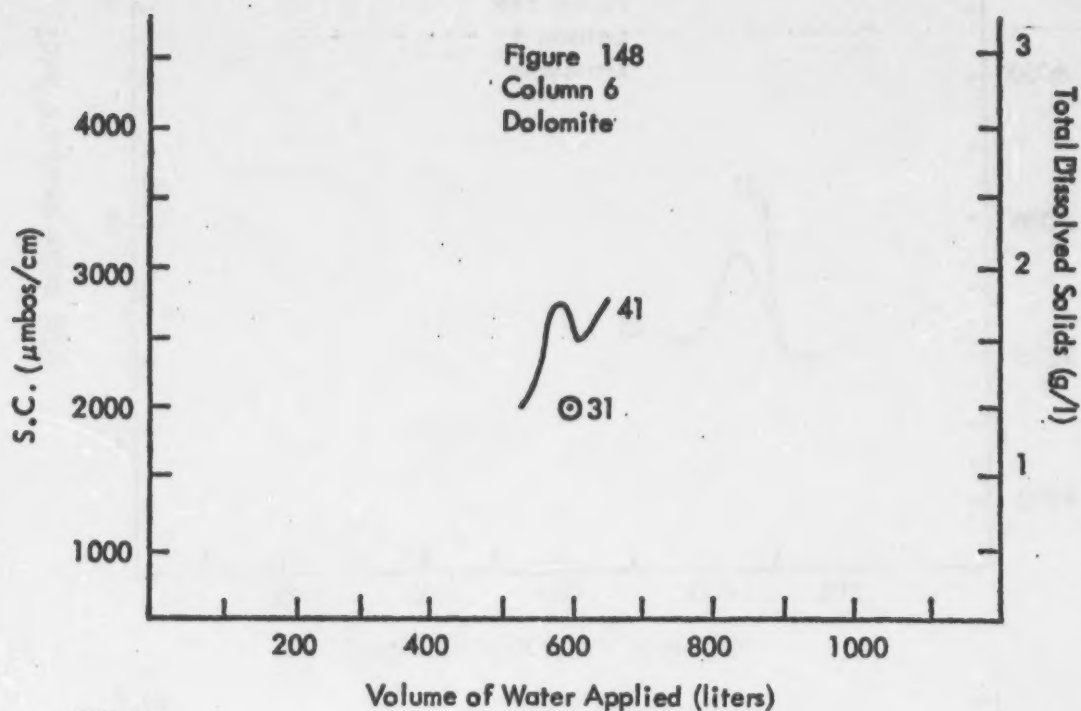
NOTE: See Figure 31 for further legend explanation.

Figures 144 and 145 Specific conductivity and total dissolved solids of leachate from Columns 2 and 3 - Limestone quarry.



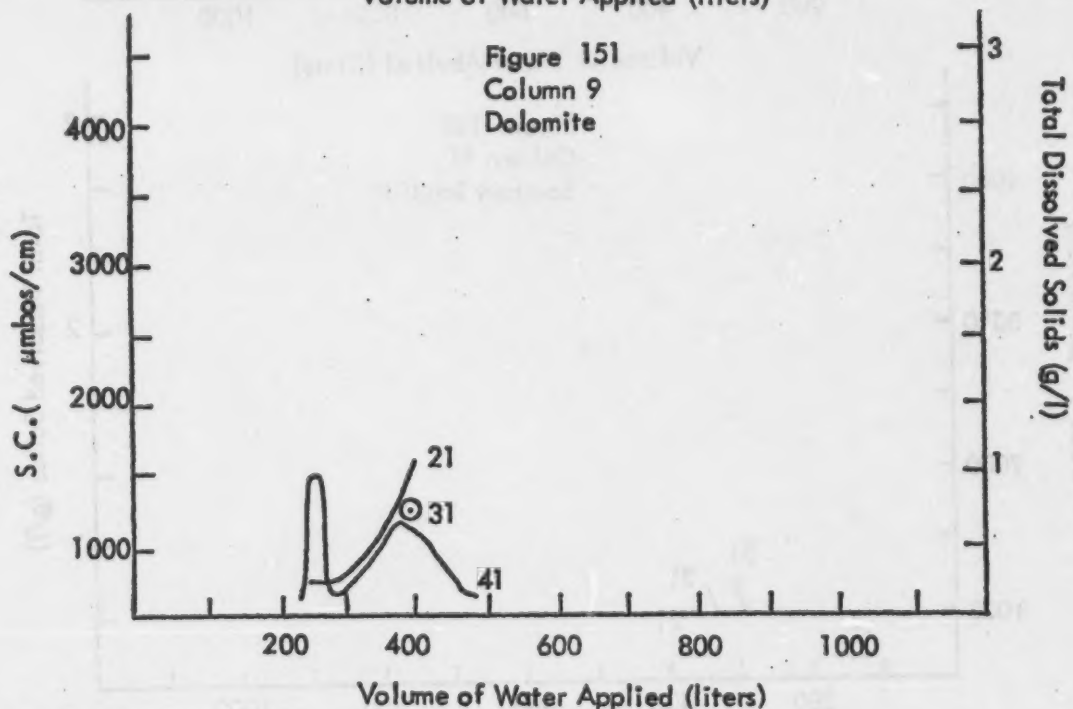
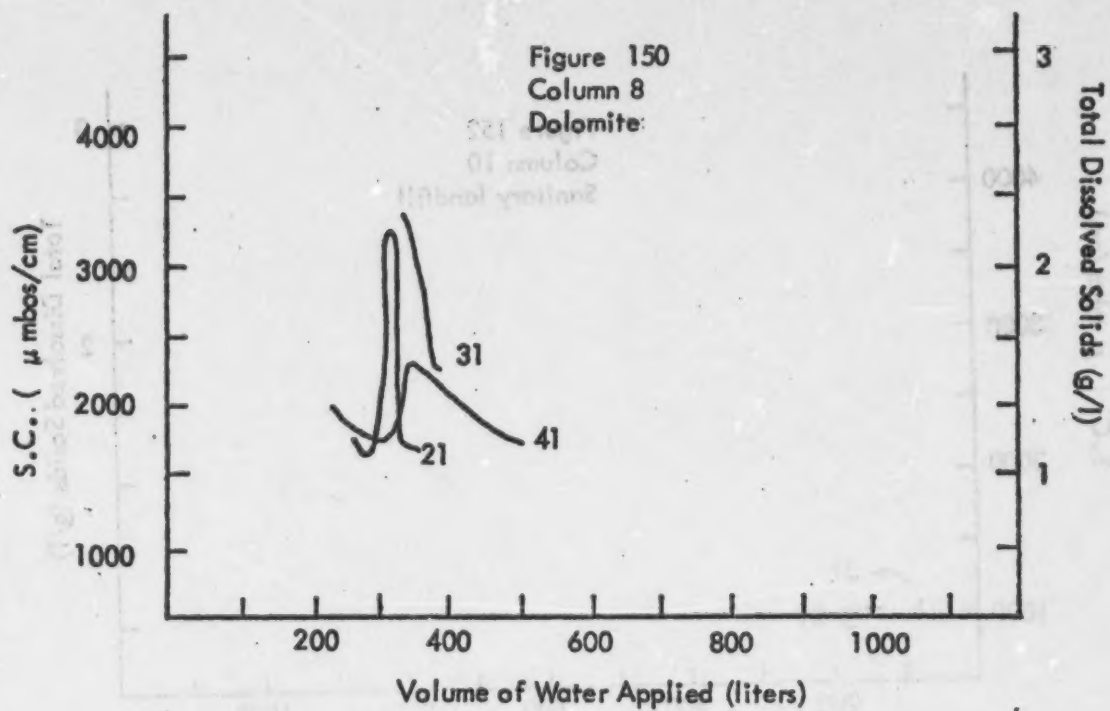
NOTE: See Figure 31 for further legend explanation.

Figures 146 and 147. Specific conductivity and total dissolved solids of leachate from Columns 4 and 5 - Limestone quarry.



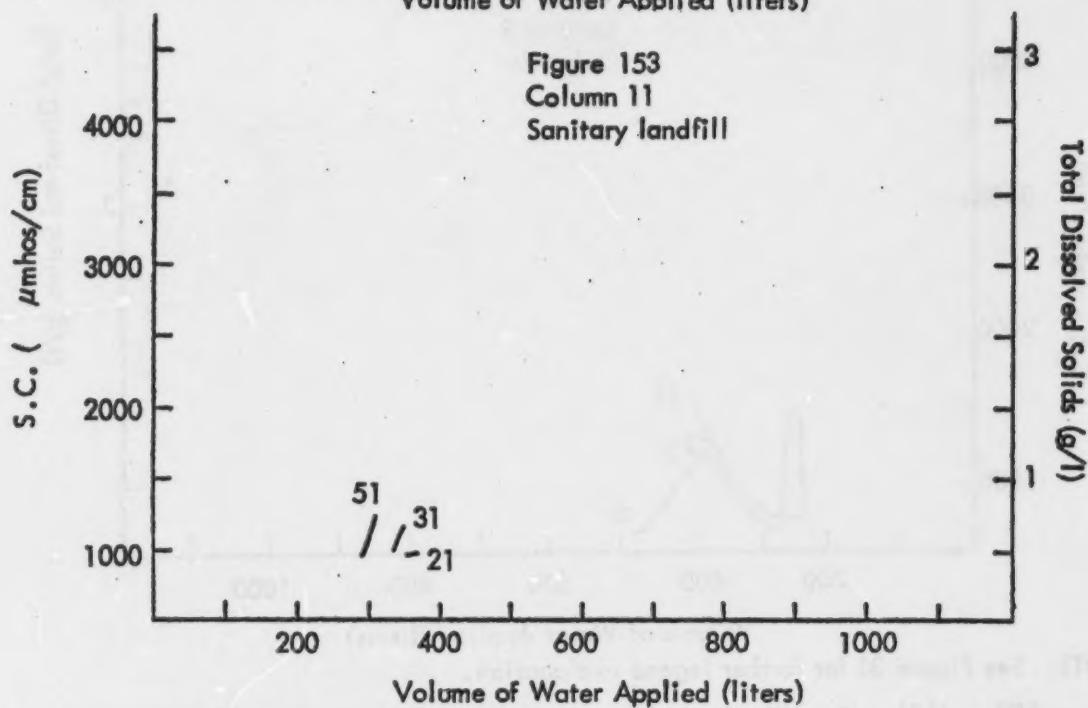
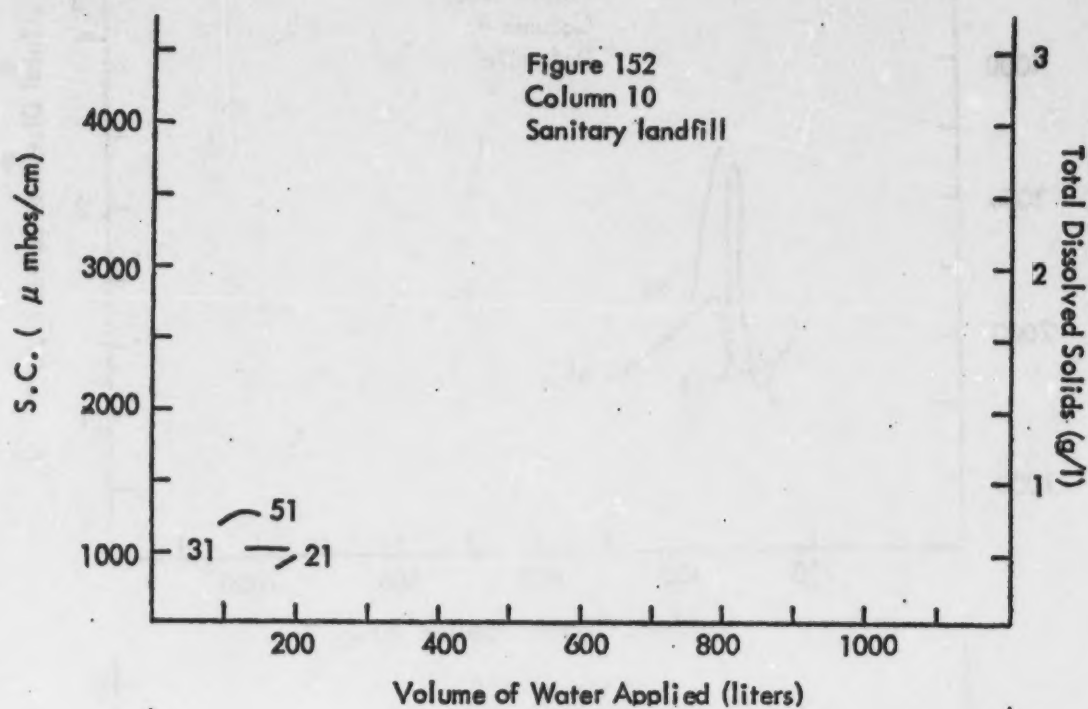
NOTE: See Figure 31 for further legend explanation.

Figures 148 and 149. Specific conductivity and total dissolved solids of leachate from Columns 6 and 7 - Dolomite quarry.



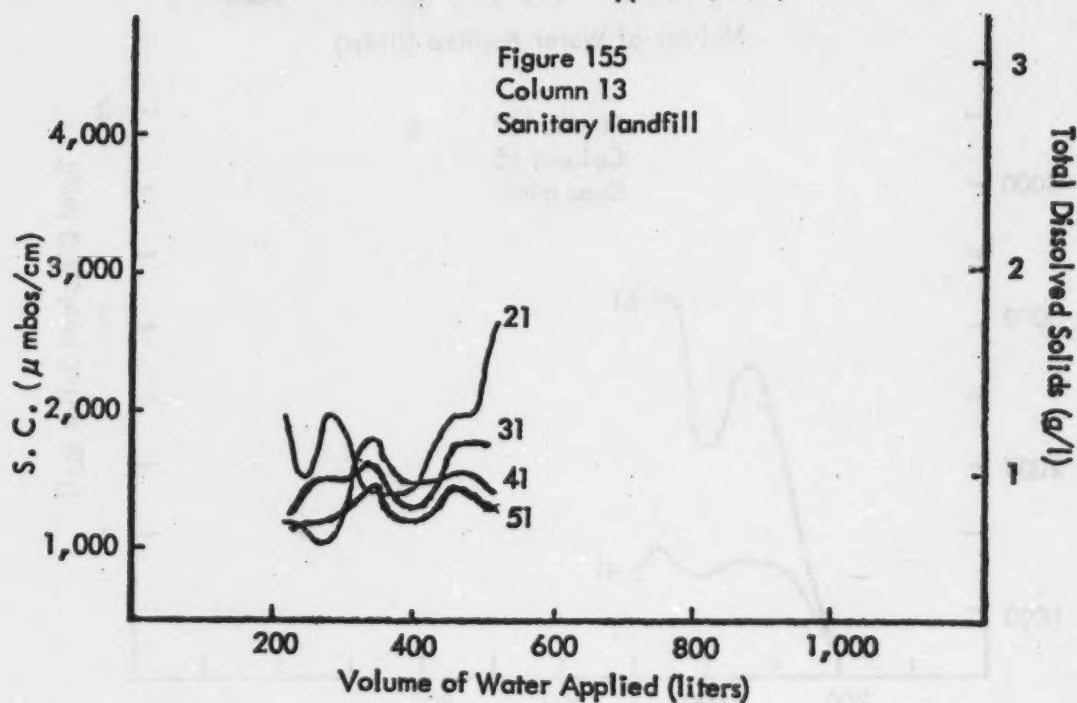
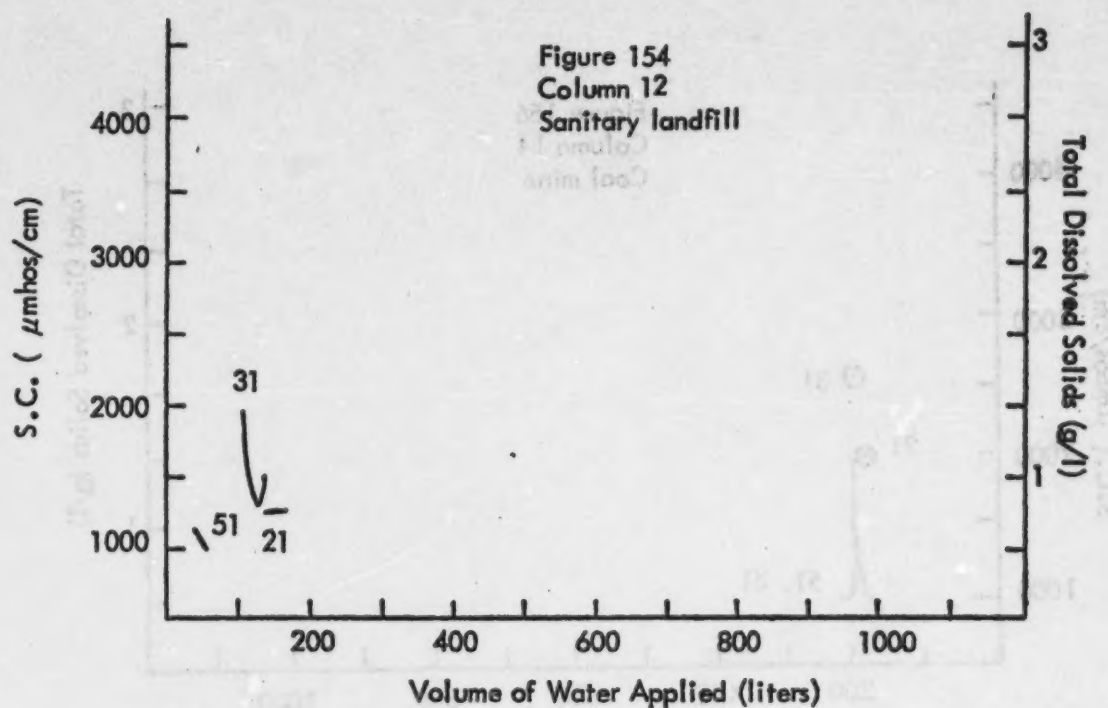
NOTE: See Figure 31 for further legend explanation.

Figures 150 and 151. Specific conductivity and total dissolved solids of leachate from Columns 8 and 9 - Dolomite quarry.



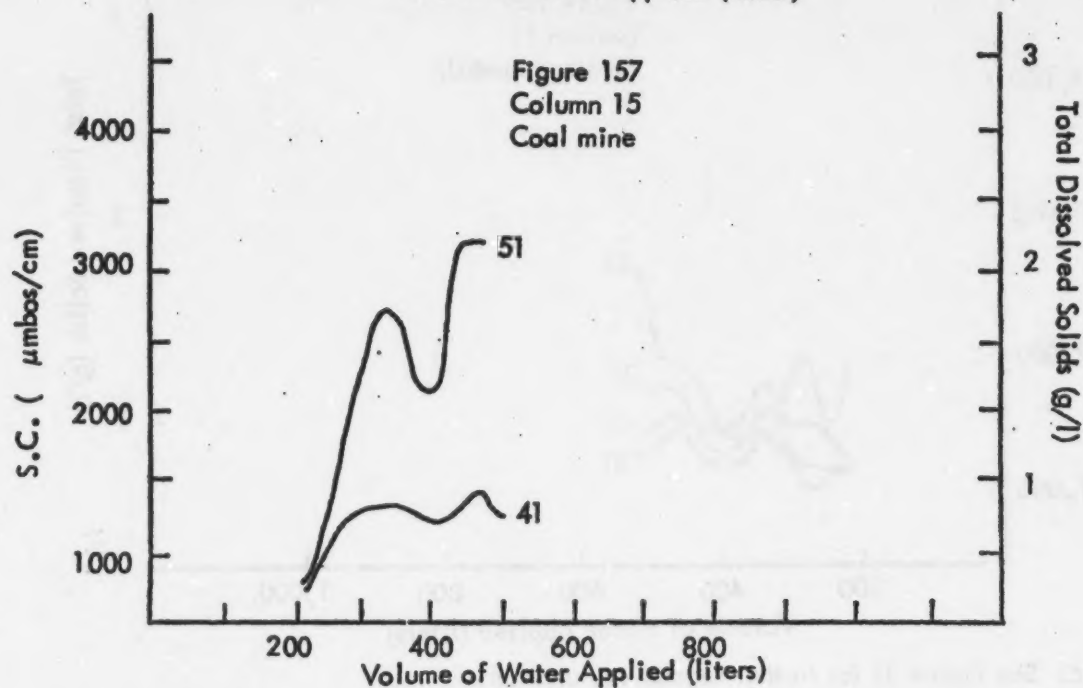
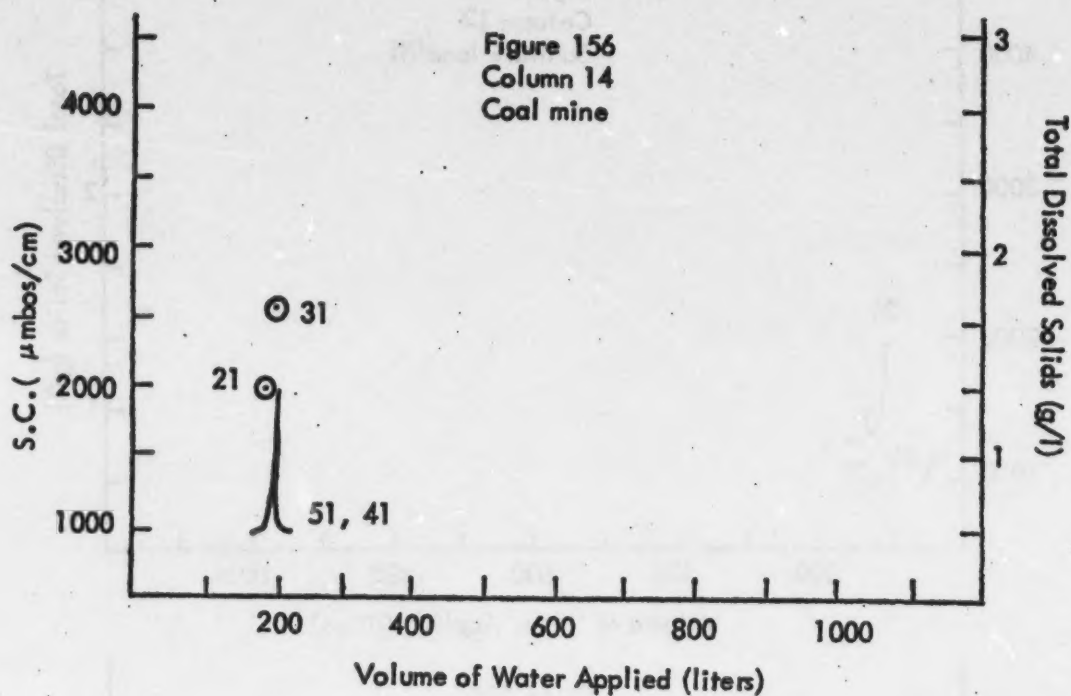
NOTE: See Figure 31 for further legend explanation.

Figures 152 and 153. Specific conductivity and total dissolved solids of leachate from Columns 10 and 11 - Sanitary landfill.



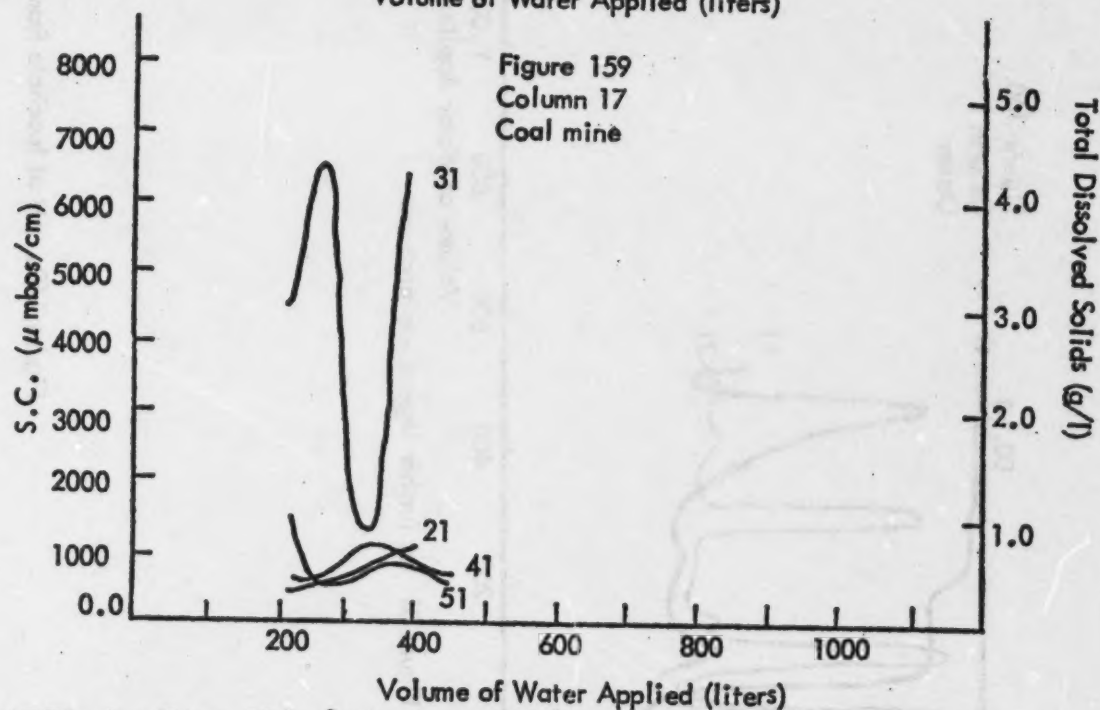
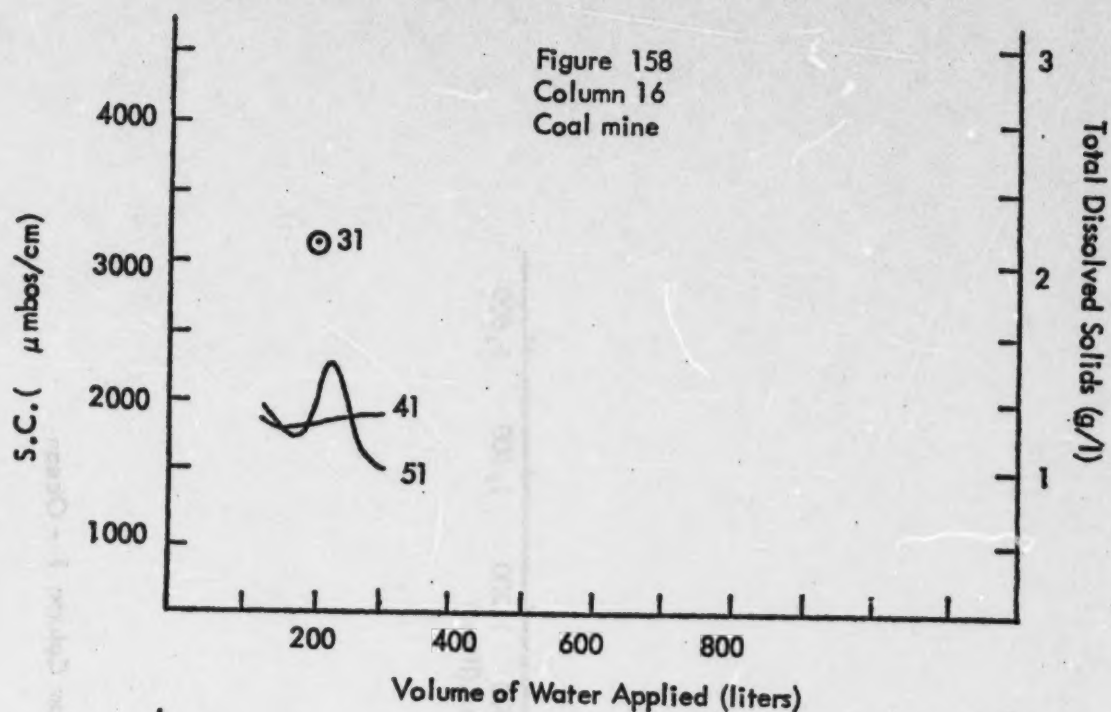
NOTE: See Figure 31 for further legend explanation.

Figures 154 and 155. Specific conductivity and total dissolved solids of leachate from Columns 12 and 13 - Sanitary landfill.



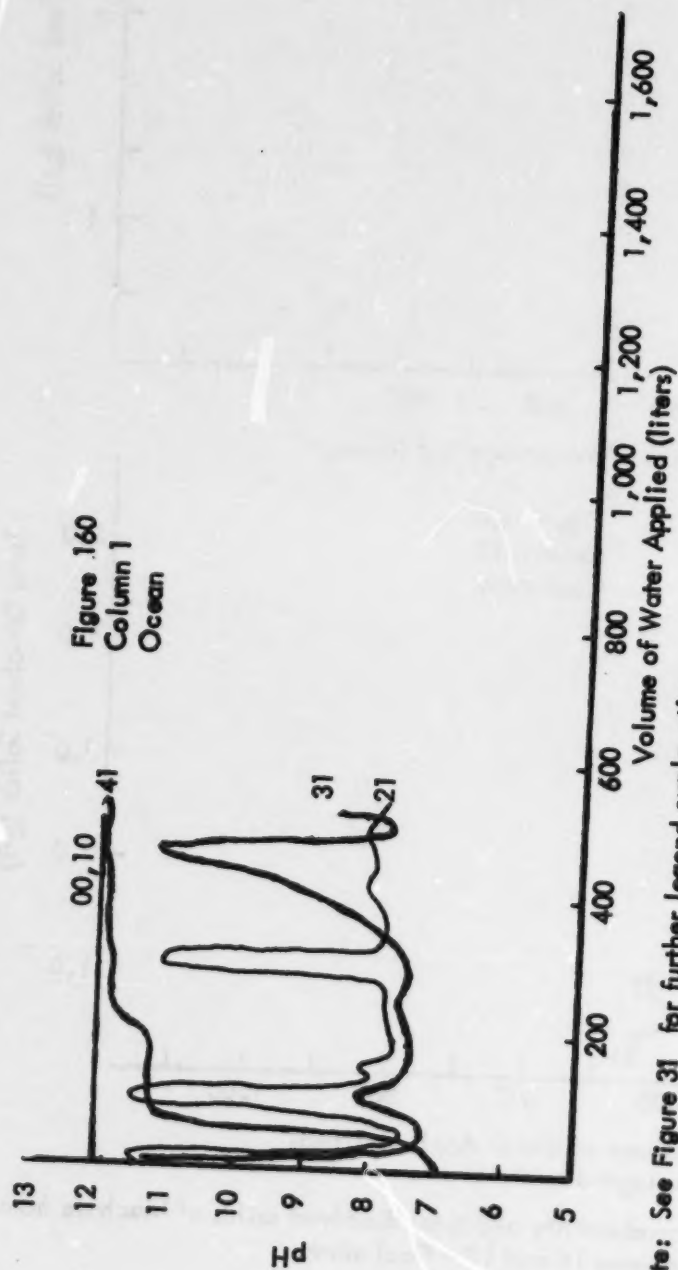
NOTE: See Figure 31 for further legend explanation.

Figures 156 and 157. Specific conductivity and total dissolved solids of leachate from Columns 14 and 15 - Coal mine.



NOTE: See Figure 31 for further legend explanation.

Figures 158 and 159. Specific conductivity and total dissolved solids of leachate from Columns 16 and 17 - Coal mine.



Note: See Figure 31 for further legend explanation.

Figure 160. pH of leachate from Column 1 - Ocean.

Figure 161
Column 2
Limestone

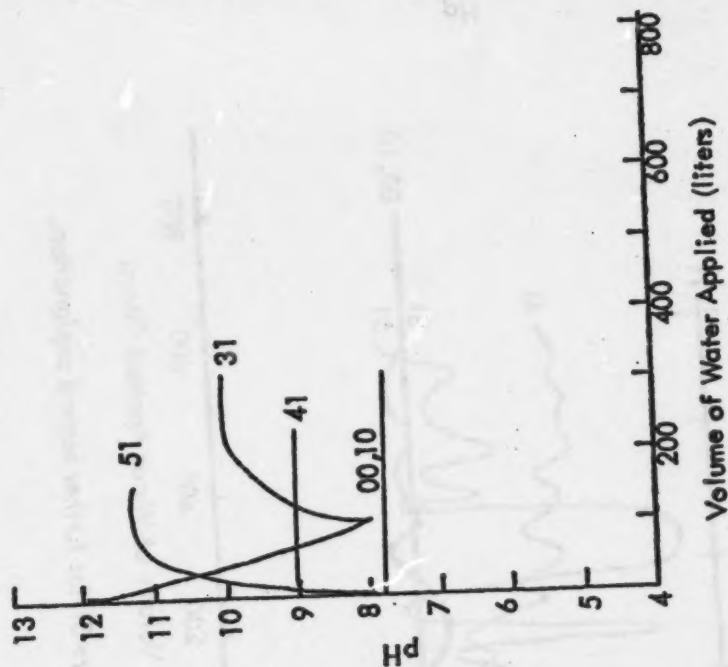
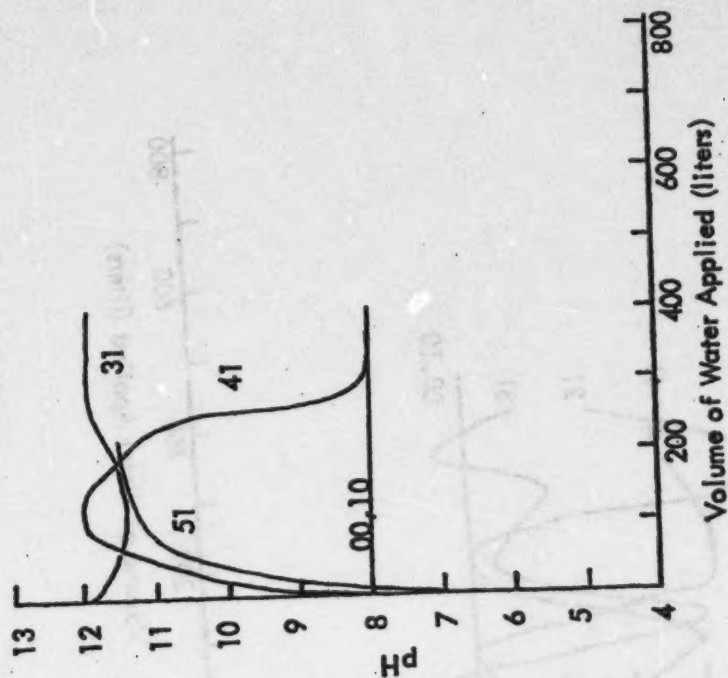


Figure 162
Column 3
Limestone



NOTE: See Figure 31 for further legend explanation.

Figures 161 and 162, pH of leachate from Columns 2 and 3 - Limestone quarry.

Figure 163
Column 4
Limestone

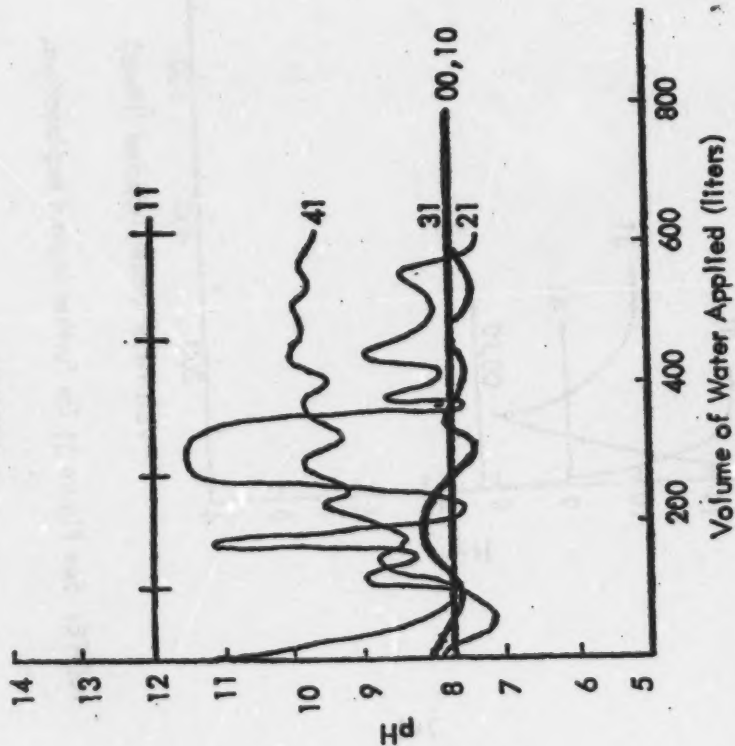
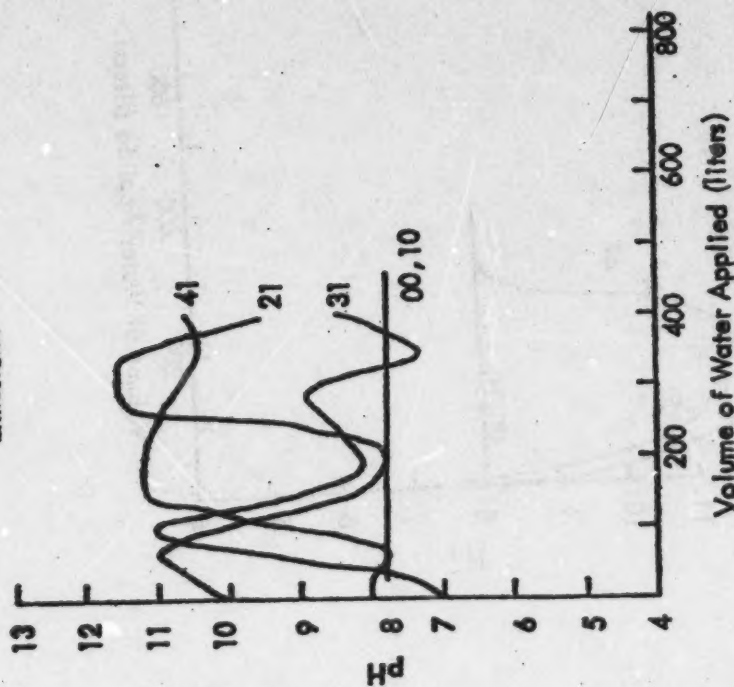


Figure 164
Column 5
Limestone



NOTE: See Figure 31 for further legend explanation.

Figures 163 and 164. pH of leachate from Columns 4 and 5 - Limestone quarry.

Figure 165
Column 6
Dolomite

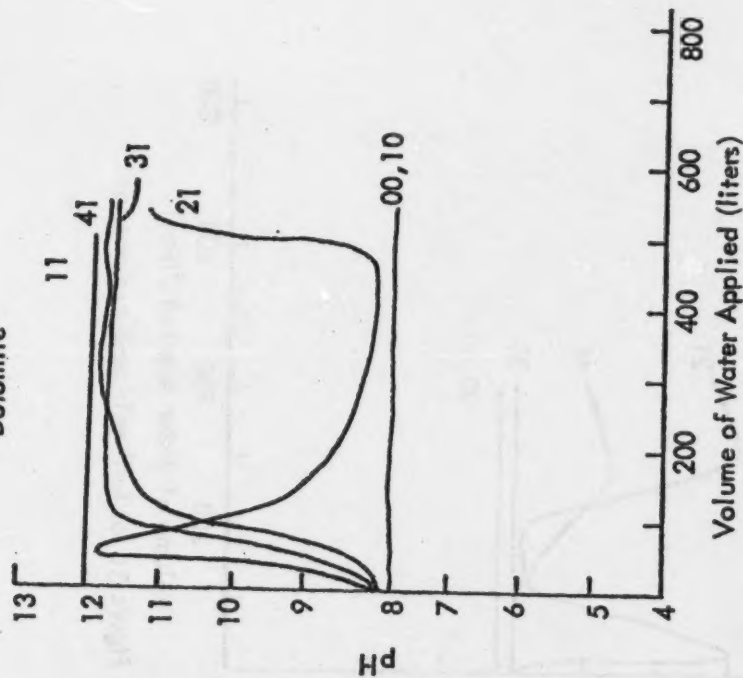
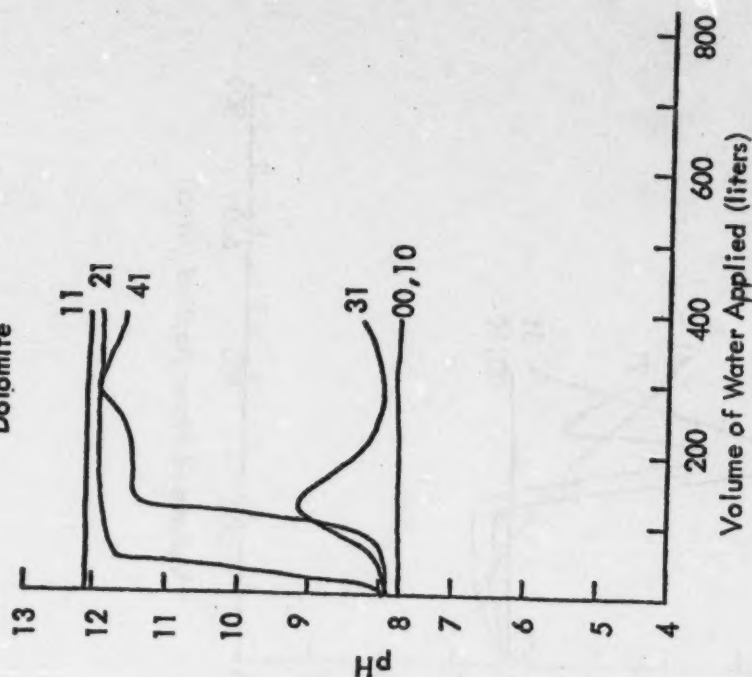


Figure 166
Column 7
Dolomite



NOTE: See Figure 31 for further legend explanation

Figures 165 and 166. pH of leachate from Columns 6 and 7 - Dolomite quarry.

Figure 168
Column 9
Dolomite

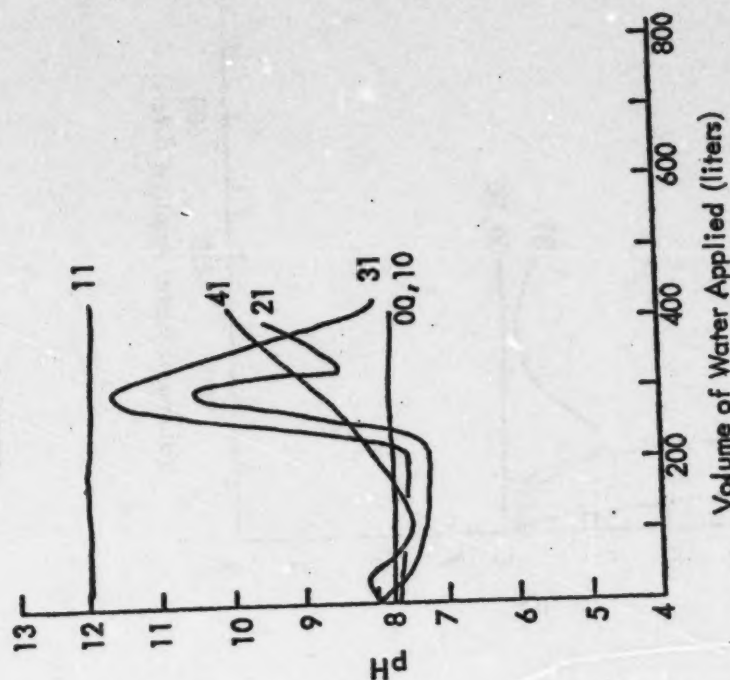
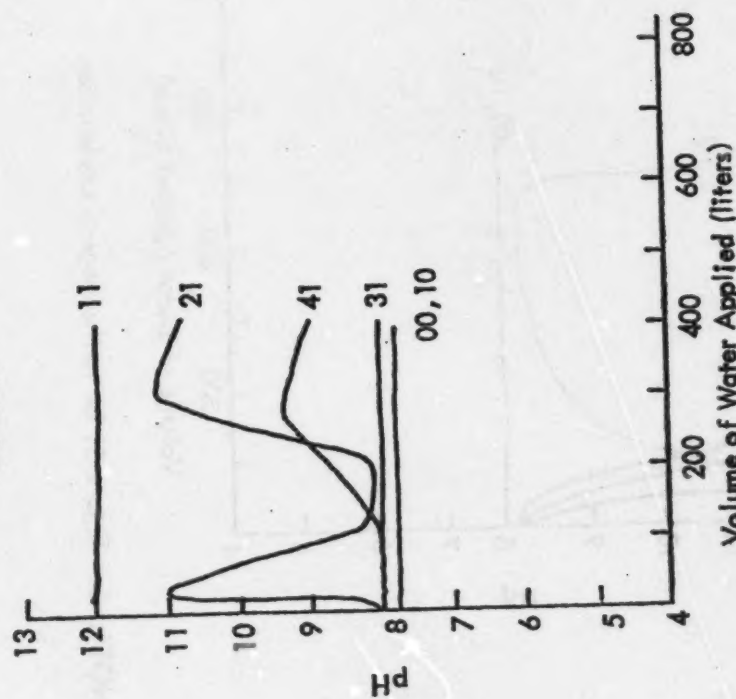


Figure 167
Column 8
Dolomite



NOTE: See Figure 31 for further legend explanation.

Figures 167 and 168, pH of leachate from Columns 8 and 9 - Dolomite quarry.

Figure 169
Column 10
Sanitary landfill

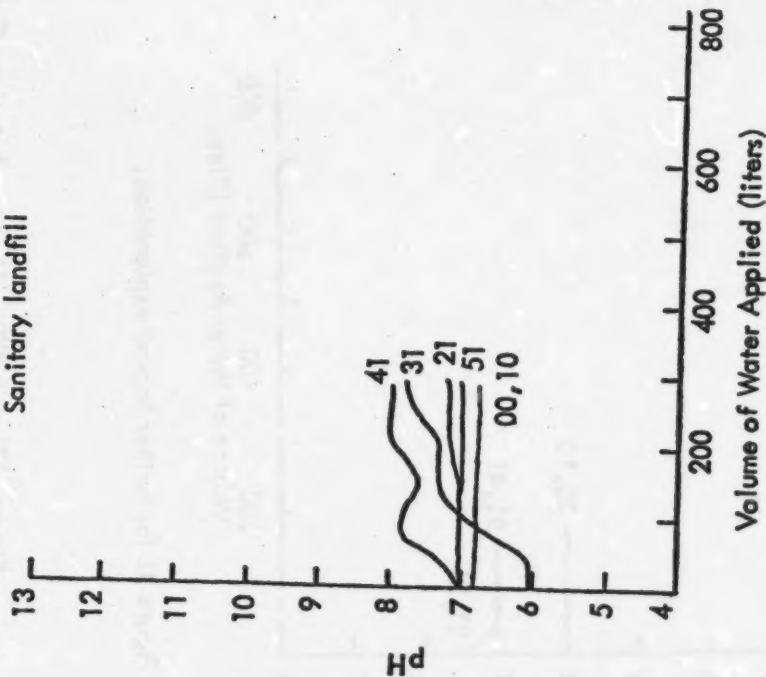
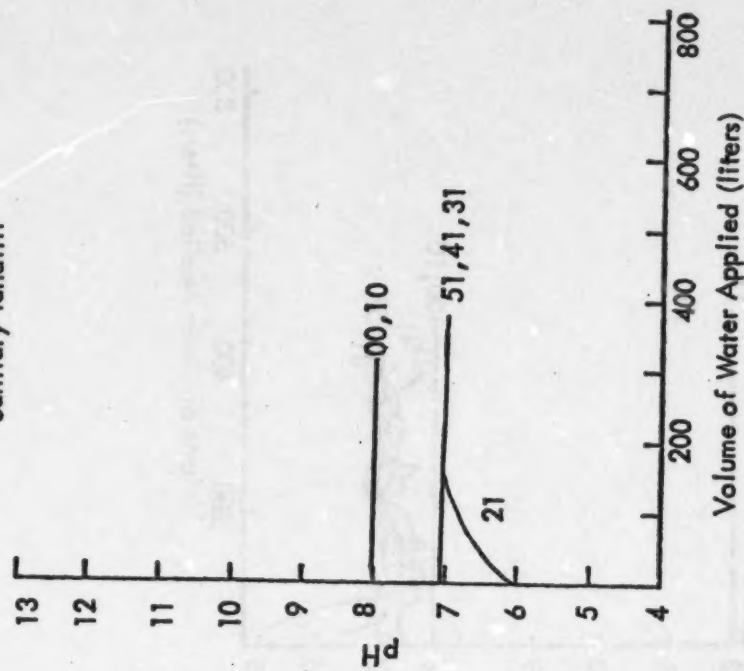


Figure 170
Column 11
Sanitary landfill



NOTE: See Figure 31 further legend explanation.

Figures 169 and 170. pH of leachate from Columns 10 and 11 - Sanitary landfill.

Figure 171
Column 12
Sanitary landfill

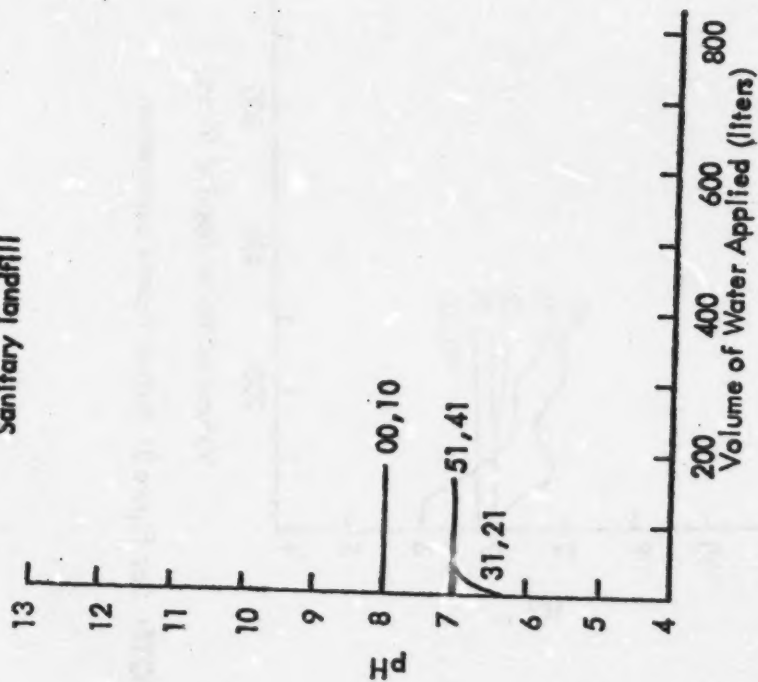
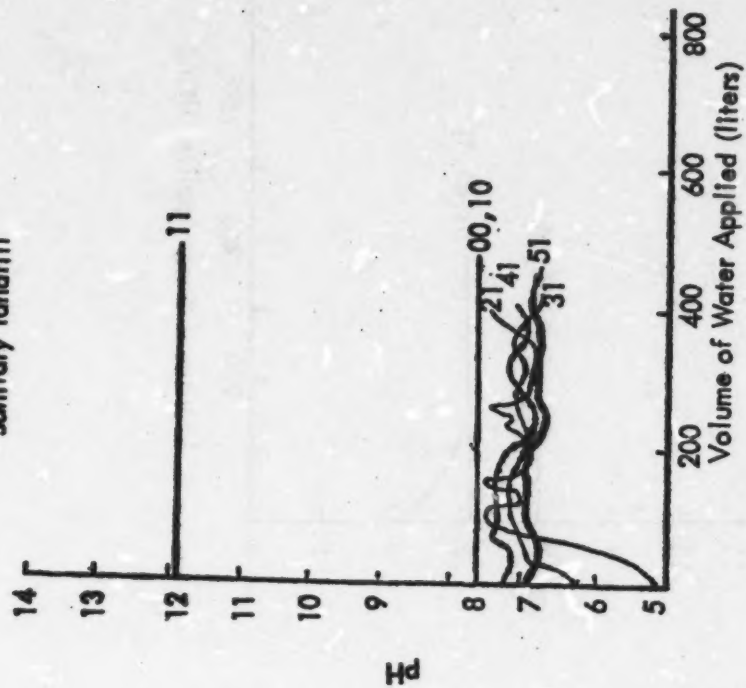


Figure 172
Column 13
Sanitary landfill



NOTE: See Figure 31 for further legend explanation.

Figures 171 and 172. pH of leachate from Columns 12 and 13 - Sanitary landfill.

Figure 173
Column 14
Coal mine

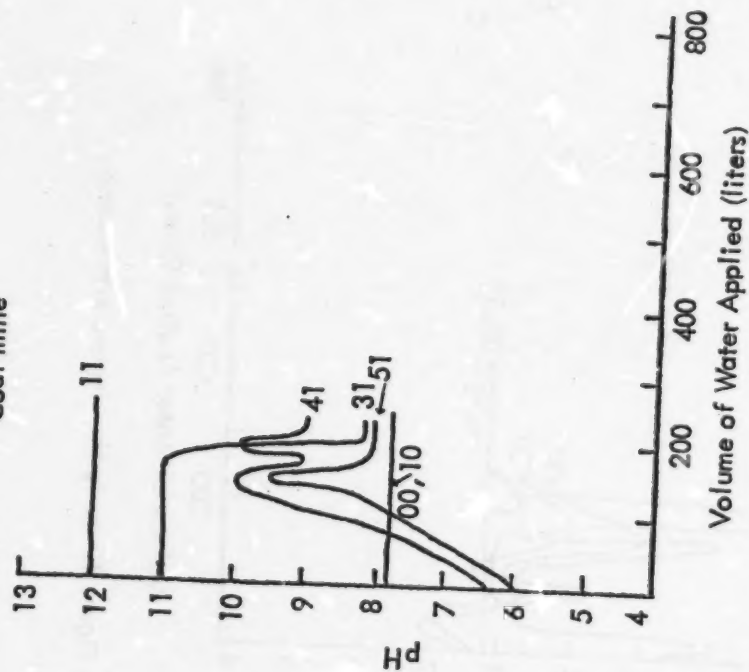
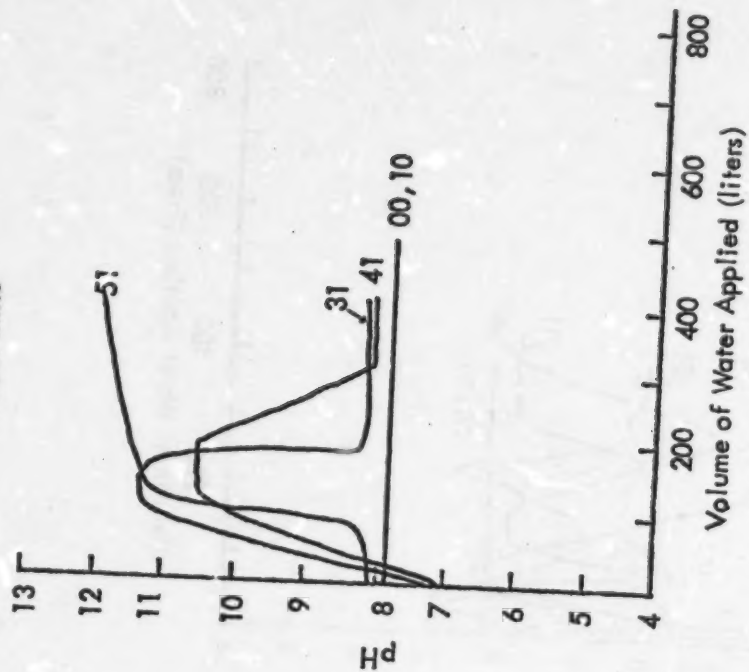


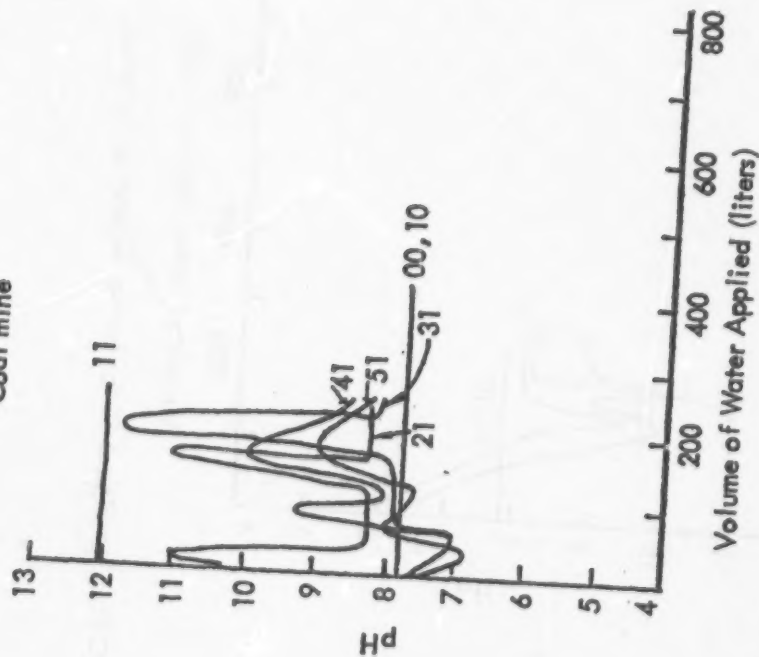
Figure 174
Column 15
Coal mine



NOTE: See Figure 31 for further legend explanation.

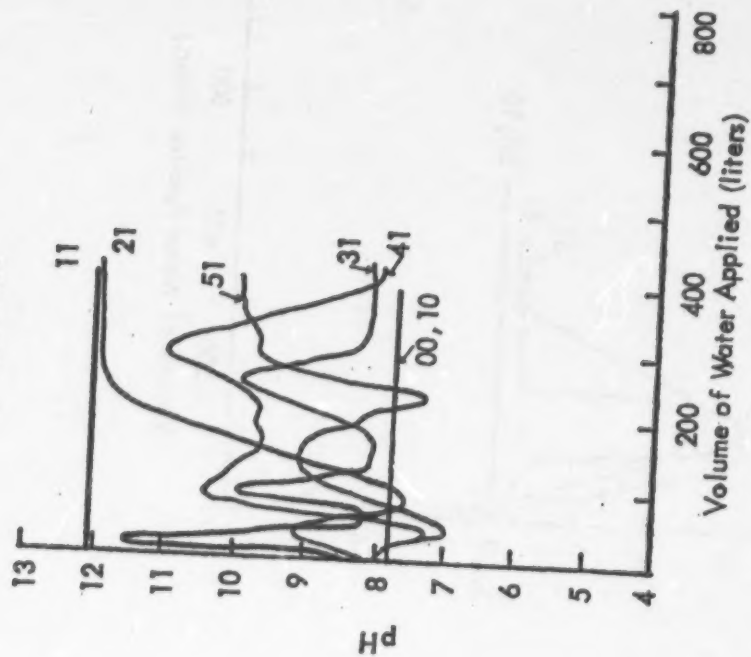
Figures 173 and 174. pH of leachate from Columns 14 and 15 - Coal mine.

Figure 175
Column 16
Coal mine



NOTE: See Figure 31 for further legend explanation.

Figure 176
Column 17
Coal mine



Figures 175 and 176. pH of leachate from Columns 16 and 17 - Coal mine.

CHAPTER 7

REUSE POTENTIAL FOR FLUIDIZED-BED RESIDUES

Introduction

Coal and oil combustion generate large quantities of residues. In 1972, for example, approximately 30 million kkg of coal residues were produced. Residue quantities are projected to increase substantially during the period 1970-90, primarily as a result of increased power demand. During that period, the electric utility industry is predicted to increase its consumption of coal by 100 percent and of oil by 150 percent.⁵⁴ Residue quantities are likely to increase more than proportionately for several reasons. First, as supplies of low-ash fuel are depleted, greater use will be made of higher-ash fuels. Second, more stringent pollution control regulations will result in fewer emissions to the environment and therefore greater solid waste process residue quantities. Third, fluidized-bed coal combustion and oil gasification methods may be adopted by a significant portion of the industry. Both once-through and regenerative limestone/dolomite fluidized-bed systems generate substantially more residues than conventional systems, although the increase is greatest with once-through systems. Preliminary work suggests that once-through systems are favored by current economics: the projected expense of regeneration (less the value of recovered sulfur products) appears to be greater than the saving from reduced limestone consumption. For coal boilers, once-through fluidized-bed systems should generate a minimum of 50 percent more residues than do conventional coal-fired power plants.⁵⁴

This chapter evaluates possible residue application areas and the market prospects for fluidized-bed residues. The following topics are considered:

- Overall reuse prospects for fluidized-bed residues.
- Review of applications for conventional coal ash and lime/limestone wet scrubber residues.
- Evaluation of specific, feasible reclamation applications of residues in concrete, asphalt, agriculture (soil amendment), soil cover (strip mines and landfills), soil cement, pozzolan cements (LFA and LCFA), acid mine drainage treatment, and road ice control.
- Preliminary assessment of market potential for residue applications.

Overall Reuse Prospects

The history of reuse for conventional coal ash provides an insight into what the utilization prospects for fluidized-bed residues might be. Relatively little of the conventional ash generated has found its way into productive use—about 16 percent in 1972. Until about 1968, the ash utilization rate had been increasing rapidly, moving from 2 percent in 1955 to 17.5 percent in 1968.⁷⁰ Since then, however, the rate has remained relatively constant,

although in total quantities reuse has continued to increase. The utilization rate has remained low even though many technically sound applications have been developed which potentially could absorb more than the annual quantities generated.⁵³ Table 52 presents estimated maximum technically feasible utilization potentials. Although many reuse applications exist, it is not likely that the utilization rate will consume the available supply in the near future.

Factors other than technical feasibility also influence actual utilization. These factors include:

- Technical complexity of the application. Potential users are less likely to adopt a new residue material if it is significantly more complicated, or if it requires major changes in production methods.
- Reliability of the new raw residue process or product.
- Sufficient information about the potential application.
- Existence of a reliable source of supply for residues or residue-based products.
- Uniformity and quality of the residue or residue-based product.

Given favorable conditions in the above areas, a potential user's decision will be based on the relative prices of conventional and residue materials, transport, and any necessary preprocessing of the residues over that required for the competing conventional material. A potential user will adopt that application which reduces his production costs and maintains desired product quality.

In comparing the magnitude of the technically feasible applications of conventional ash with actual utilization, there are indications of substantial economic and other impediments to greater increased use. Many of these barriers may be overcome in time, but unless further reuse incentives are provided, most of the increased residues generated for 1970-90 will not be reused, but instead, will require disposal. This conclusion must be modified for fluidized-bed residues, however, since their composition and characteristics are substantially different from those of conventional combustion ash residues. This is illustrated in Tables 53 and 54, which compare the composition of conventional coal ash, modified ash (MFA), and fluidized-bed ash. Lime or dolomite modified fly ash is generated by flue gas desulfurization (FGD) systems (e.g., wet limestone scrubbers) and fluidized-bed combustors. Since differences affect the suitability of a residue for a given application, it is difficult to predict the successes or failures of FBC residue applications. The FGD residues (particularly those from dry systems) are quite similar to fluidized-bed residues. Hence, the reuse potential of FGD and fluidized-bed residues may be compared with some reliability.

There is considerable literature on applications for residues from conventional coal combustion, from municipal waste incineration, and from lime-limestone scrubbing (frequently used for air pollution control on coal-fired generating units). In addition, there is

TABLE 52. ESTIMATED ASH UTILIZATION POTENTIAL (10^6 kkg/yr)

Use	Maximum Utilization Technically Feasible	1970 Utilization	Estimated Utilization 1971 Conditions	Potential Improved Utilization
Fly ash concrete (structural, mass and concrete products)	9-14	0.49	3.2	5.4
Lightweight aggregate	12	0.19	0.5	2.7
Raw material for cement clinker	12	0.15	0.23	---
Bricks	9	---	---	---
Filler in bituminous products	1-2	0.12	0.68	---
Base stabilizer for roads (AP ^a)		0.10	0.3	> 9.1
Agriculture and land recovery (AP)	---	---	---	---
Control of mine subsidence and fires	> 1	0.01	0.68	> 0.9
Structural fill for roads construction sites, land, reclamation, etc. (AP)	---	0.29	0.5	---
Others	---	0.15	0.23	---
Total	---	1.50	6.3	---

^aAP - annual production.

Source: 130.

TABLE 53. COMPARISON OF ASH COMPOSITION (%)

Constituent	Coal Ash	Lime Modified Ash	Dolomite Modified Ash	Lignite Ash
SiO ₂	49.10	30.85	30.81	32.60
Al ₂ O ₃	16.25	13.70	12.54	10.70
Fe ₂ O ₃	22.31	11.59	10.72	10.0
TiO ₂	1.09	0.68	0.42	0.56
CaO	4.48	33.58	17.90	18.00
MgO	1.00	1.49	14.77	7.31
Na ₂ O	0.05	1.12	0.72	0.87
K ₂ O	1.42	0.71	0.99	0.68
SO ₃	0.73	2.20	8.09	2.60
C	2.21	1.12	1.76	0.11
H ₂ O soluble	2.51	22.11	--	8.55

TABLE 54. COMPARISON OF FBC RESIDUE COMPOSITIONS

Constituent	Ash Composition (%) ^a		
	Exxon Miniplant	Pope, Evans and Robbins Plant	Esso, England Gasifier
Fe ₂ O ₃	9.99	15.71	0.02
CaO	13.44	4.9	10.5
MgO	0.61	0.32	0.07
SO ₃	5.81	4.56	6.22
H ₂ O soluble	0.21	0.42	

^a These values do not sum to 100 percent. The remainder is primarily silicon dioxide with traces of unburned carbon and metal oxides.

Source: 42.

literature for proposed or experimental uses.

Types of Coal Ash

There are three types of residues collected from coal combustion: fly ash, bottom ash, and slag. Fly ash is the ash collected from the stack effluent; bottom ash and slag are the residues collected from the bottom of the boiler. Whether these bottom residues are an ash or a slag depends on the design of the particular boiler. For any specific boiler unit the fly ash and bottom ash will have a similar chemical composition, except that the bottom ash will be lower in carbon content.

Physically, fly ash consists of finely divided spheroids of siliceous glass ranging from 1 to 50 microns in diameter. Some of these spheroids are considerably finer than portland cement, and a minor fraction consists of larger, irregularly shaped particles, some opaque and some transparent or translucent. Carbon is present chiefly in the form of irregularly shaped particles of coke. Depending upon the type of coal and combustion conditions, the carbon content of fly ash in the United States ranges from less than 1 to more than 20 percent. The physical and chemical characteristics of fly ash emitted from any combustion chamber depends on the type of combustion equipment and its design; the combustion or firing rate; the oxygen ratio, burning characteristics, and particle size of the coal; variations in steam load, draft, and combustion controls; and operator skill. About 70 percent of the coal ash residue is collected as fly ash.

The bottom ash is collected either as an ash or slag depending on the particular boiler design. The ash is grey to black in color, quite angular, and has a porous surface. The slag particles are normally black, angular particles having a glass appearance. The bottom ash particles have an average particle diameter size of 2-1/2 millimeters and an average specific gravity of about 2.5. When there are reuse markets for fly ash, it is handled dry by a pneumatic system, stored in silos or bins on the plant site, and then transported in closed tank trucks or rail cars. Slags to be sold are pumped from quench tanks below the boiler to draining bins and then are generally stored in piles until marketed. Bottom ash and slag are granular materials and lend themselves to mechanical handling schemes.

Pulverized coal-fired units are "wet" or "dry" bottom, with the amount of fly ash and bottom residue in each related to furnace design and the pulverization level, volatile matter, and ash content of the coal. In the wet bottom design, up to half of the total ash can be trapped within the furnace as ash or slag; however, bottom ash in "dry" bottom units amounts to only 20-25 percent of the total ash.

Coal Ash Utilization

United States.

Table 55 compares ash generation and use; in 1972 only about 16 percent of the ash

TABLE 55. COMPARATIVE ASH PRODUCTION AND UTILIZATION, 1966-1972

Production (kkg)	1966	1967	1968	1969	1970	1971	1972
Fly ash	15,533,855	16,701,139	17,974,729	20,234,314	24,074,886	25,175,333	28,855,791
Bottom ash	7,317,065	8,283,915	6,585,446	7,295,595	8,972,920	9,125,341	9,682,256
Boiler slag	--	--	2,317,466	2,739,954	2,541,455	4,509,421	3,430,664
Total	22,850,920	24,985,053	26,877,641	30,269,863	35,589,261	38,810,095	41,968,711

Utilization	1966	1967	1968	1969	1970	1971	1972
Total (kkg)	2,767,520	3,442,507	4,711,932	4,814,215	4,622,704	7,805,163	6,872,381
Fly ash (%)	7.9	8.2	9.6	8.13	8.13	11.7	11.4
Bottom ash (%)	21.0	25.0	25.0	25.0	18.63	16.03	24.3
Boiler slag (%)	--	--	57.8	57.8	39.06	75.21	35.3
Total (%)	12.11	13.78	17.53	15.90	13	20	16.3

Source: 88.

and slag produced found application (11.4 percent of the fly ash, 24.3 percent of the bottom ash, and 35.3 percent of the boiler slag). Ash collection and utilization for a typical year (1971) are shown in Table 56; estimated 1976 ash generation is included for comparison. The main applications were as an additive to cement, a fill material for road and other construction, and a filler in asphalt mix. The "miscellaneous" use category was also quite large; Table 57 lists some of the applications aggregated under that heading. It can be inferred that a large quantity of residues was removed at no cost to utilities and found its way into useful applications. Some of these applications (and known quantities) are listed in Table 58.

Yearly fluctuations in coal ash used suggest that the trends are influenced by market factors; thus, valid projections for future consumption are difficult to make. Boiler slag has been found useful in increasing the skid resistance of asphalt pavement. The use of coal ash as a raw material in the manufacture of portland cement is another application where usage has increased in the past several years. Recent research results indicate that large quantities of coal ash could also be effectively used for agriculture and land reclamation products. The use of coal ash as a raw material in the manufacture of portland cement is another application where usage has increased in the past several years. Recent research results also indicate that large quantities of coal ash could also be effectively used for agriculture and land reclamation products. The use of coal ash for lightweight aggregate initially looked promising, but in the last few years its use has declined.

Effective utilization of coal ash requires that the ash satisfy the technical specifications for the application and be economically competitive. Ideally, any production or utilization process should be located close to the source of raw material; that is, at the power plant. However, this is not always possible. Thus, transporting coal ash to where it is to be used is a major economic factor. Using trucks, fly ash can be transported from a source at an average 1976 cost of \$0.04 per kkg/km (18 to 27 kkg per truck). The cost of loading and unloading is about \$2.00 per truck load. Furthermore, trucks can be expected to operate with maximum economy only to a range of about 150 to 175 miles, depending on road conditions. This enables the trucker to get to his destination, unload, and return in the same day, avoiding any overtime or stayover.

Fly ash used in cement and concrete applications competes with natural raw materials and cement industry products. Its use is hampered by the fact that 1976 freight rates for shipping fly ash are about 20 percent higher than for the natural products. This is because of tariffs that give an advantage to natural or virgin materials over secondary materials.

Europe.

In 1971, the Federal Republic of Germany was using 79 percent of its total ash production of 6,500,000 kkg, France was using 65 percent of its production of 4,185,000 kkg, and the United Kingdom was using 54 percent of its production of 10,370,000 kkg.¹³² The principal uses of the coal ash were in road construction, compacted concrete, and construction site fills.

TABLE 56. ASH COLLECTION AND UTILIZATION, 1971

	Fly Ash (kkg)	Bottom Ash (kkg)	Boiler Slag (kkg)
Ash utilized:			
Mixed with raw material before forming cement clinker	94,550	NA ^a	83,440
Mixed with cement clinker or mixed with cement (pozzolan cement)	15,001	NA	NA
Partial replacement of cement			
Concrete products	160,725	32,094	68,551
Structural concrete	168,256	NA	NA
Dams and other massive concrete	64,784	NA	NA
Lightweight aggregate	162,294	12,648	NA
Fill material for roads, construction sites, etc.	329,663	484,156	2,384,924
Stabilizer for road bases, parking areas, etc.	33,511	7,149	44,964
Filler in asphalt mix	133,953	2,570	74,118
Miscellaneous	89,633	431,299	388,305
Total	1,252,370	969,916	3,044,302
Ash removed at plant site at no cost to utility but not covered in categories listed under "ash utilized"	1,698,938	492,514	346,346
Total ash utilized	2,951,308	1,462,430	3,390,648
Ash removed to disposal areas at company expense	22,224,448	7,663,065	1,117,941
Total ash collected	25,175,756	9,125,495	4,508,589
Estimated 1976 ash production	33,561,352	10,651,580	2,284,060

^a Not applicable.

Source: 31.

TABLE 57. KNOWN MISCELLANEOUS USES FOR ASH AND SLAG

Oil well cementing	Oil well drilling
Mine fire control	Industrial testing
Mine subsidence control	Vanadium recovery
Neutralization of acid mine drainage	Ice control
Cleaning abrasive	Outdoor school tracks
Spontaneous combustion control	Asphalt shingles
Highway bridges	Sandblasting grit
Test caps	Filler for glass
Refractory add mix	Filler for fertilizer
Insulating cement	Filler for paint
Grouting	Filler for plastics
Snow sanding	Dike repair and buildings
Pipe coating	Drainage filter
Foundries	Aggregate
sand	Landfill
manufacturer products	Agriculture
Chemical products	Dust control
Poz-O-Pac ^a	Seal coating
Sewage treatment plants (filtration)	Roofing granules
Substrate course (heavy construction)	Railroad base
Ready mix	Mineral wool production

^a A pozzolan.

Sources: 1, 2, 4, 23, 26, 29, 31, 33, 34, 37, 40-42, 46, 50, 53, 54, 59, 68-70, 80-82, 96, 101-103, 110, 111, 114, 116-118, 126, 128-131, 139, 140, 143-154, 167, 189.

TABLE 58. KNOWN USES FOR ASH REMOVED FROM PLANT
AT NO COST TO UTILITY, 1971

Application	Fly Ash (kkg)	Bottom Ash (kkg)	Boiler Slag (kkg)
Manufacturing cement	46,900	N ^a	N ^a
Mine fire control	75,250	35,325	N ^a
Antiskid winter roads		161,775	150,714
Building blocks and fill material	N ^a	13,373	N ^a
Experimental soil condition	23	N ^a	N ^a
Miscellaneous fill material	433,567	31,534	208,105
Airport pavement	14,697	N ^a	N ^a
Soil stabilization	4,568	N ^a	N ^a
Fertilizer filler	1,198	N ^a	N ^a
Rubber filler	269	N ^a	N ^a
Vanadium recovery	181	181	N ^a
Dust control	N ^a	10,237	N ^a
Asphaltic wear course aggregate	N ^a	N ^a	1,932
Total	693,916	252,425	360,751

^aNot applicable.

^bNot available.

Source: 31.

About 22 percent of the total amount of ash used was employed in road construction, mainly in France and the United Kingdom. Eighteen percent of the total was used in concrete. Construction filler accounted for about 28 percent of the total used. Miscellaneous uses included coal mine fire control, addition of fly ash to foundry sand, use as a component of blasting compounds for cleaning metal surfaces, manufacture of acoustical block, pesticides, soap, etc. Table 59 gives the figures for hard coal and lignite ash production and utilization in Europe and the United States in 1967, 1969, and 1971. Annual fly ash production in the United Kingdom is approximately 10 million kkg. The low density ash is useful for road fill, especially when embankments have to be constructed over poor ground support such as compressible alluvial clay or silt. In such situations, excessive road foundation weight could produce settlement beyond allowable limits and may even produce a complete failure of the subsoil foundations.

In England the wet weight of fly ash per compacted cubic meter is between 1.17 and 1.44 kkg/m³ depending on the source and moisture content of the material. This compares favorably with the weight of traditional (British) fill material. Table 60 gives a comparison of fly ash densities with other traditional fill materials.

The stability of fly ash is such that it is now being used in Great Britain behind bridge abutments, etc. Fly ash, being pozzolanic, has both a high angle of shearing resistance and high cohesion. The relatively high shear strength of fly ash together with its low density suggests its use as a support edge for selected filling behind earth retaining structures. Being both granular and porous, it is also an excellent drainage medium. Because of its self-hardening properties, there is little settling in the compacted fly ash. Being light and fine, fly ash can be readily transported without special equipment, even in confined areas.

Fly ash is being used throughout the United Kingdom and other European countries for load-bearing structural fills at industrial, schools, and other sites since it has excellent load-bearing and foundation strength. Furthermore, because of its low density and self-hardening capacity, fly ash makes an ideal stabilized sub-foundation support for buildings built on unstable ground. Because it is self-hardening, fly ash is ideal for trenching, as deep neat trenches can be excavated using minimal trench supports. An ash fill, after hardening, is excellent material for trimming and so it is ideal for excavating pad foundations, manholes, utilities, etc. Small to medium-sized rollers of the vibrating type can compact fly ash adequately. Ash is inert and alkaline. Although tests have demonstrated few adverse effects on cast iron, lead, copper, PVC, or glazed stoneware pipes embedded in ash fills, it is important to remove soluble salts from new ash to prevent electrolytic metal corrosion or water pollution.

Specific Applications for Coal Ash

This section considers the following specific application areas for coal ash:

- Concrete
- Stabilized bed construction

TABLE 59. DEVELOPMENT OF ASH PRODUCTION AND USE IN THE
ECONOMIC COMMISSION FOR EUROPE REGION^a

Ash Source	Production (10 ³ kkg)	1967			1969			1971		
		Use		Production (10 ³ kkg)	Use		Production (10 ³ kkg)	Use		Production (10 ³ kkg)
		Amount (10 ³ kkg)	% of Production		Amount (10 ³ kkg)	% of Production		Amount (10 ³ kkg)	% of Production	
Hard coal										
Europe	27,250	12,477	45.3	35,710	13,630	34.8	59,922	15,983	26.7	
U. S. A.	27,500	3,744	13.6	31,661	4,862	15.3	42,781	8,604	20.1	
Total	54,750	16,221	29.6	67,371	18,482	27.5	102,703	24,587	23.9	
Lignite										
Europe	21,370	1,380	6.4	23,017	1,278	5.5	36,353	1,658	4.6	
U. S. A.	400	6	1.5	NA ^b	NA	NA	449	18	4.1	
Total	21,770	1,386	6.4	23,017	1,278	5.5	36,802	1,676	4.6	

^a The UN Economic Commission for Europe (ECE) is composed of 32 countries in the European geographical region and the U.S.A. Its purpose is to present economic collaboration among all those countries.

^b NA - Not available.

Source: 132.

TABLE 60. DENSITY OF FLY ASH COMPARED WITH TRADITIONAL FILLS

Material	Compacted Density (kkg/cu m)
PFA	1.1 - 1.3
Limestone	1.6 - 2.0
Burnt colliery shale	1.7 - 2.0
Sand	≤ 2.10
Clay	≤ 1.77
Hoggin (sand/clay)	≤ 2.14
Chalk	≤ 1.75

Source: 137.

- Fill material
- Agriculture and reclamation
- Brick manufacture
- Water quality improvement
- Miscellaneous

Current and experimental applications are considered.

Concrete.

The addition of fly ash to concrete can improve its strength, resistance to sulfate attack, workability, and permeability; it may also help control shrinkage and evolution of heat during setting. Fly ash concrete reportedly clings less tenaciously to form, and retains sharper corners and details, thus enhancing the concrete's architectural value.

Fly ash is valuable in cement and concrete primarily because it is a pozzolan. Pozzolans are siliceous-aluminous materials that have little or no cementitious value themselves, but, in finely divided form and in the presence of moisture, are able to react chemically with calcium hydroxide and other alkaline earth hydroxides to form compounds that harden. Fly ash in concrete also acts as a mechanical filler supplementing or replacing fine (sand) aggregate. Its spherical shape improves the workability of the plastic concrete and the ease with which it is finished.²⁰ In domestic sewers, concrete is frequently exposed to attack by sulfuric acid formed through the contact of hydrogen sulfide with wet surfaces. Addition of fly ash to concrete mixes can materially increase a concrete's resistance to sulfuric acid attack.

Most fly ash concretes require more air-entraining agent to achieve a similar air content to that required for regular concrete. Entraining agent requirements for a constant air content increase with the percentage of fly ash and its carbon content present as a replacement for portland cement.

Specifications for fly ash in concrete, bituminous pavement, and light-weight aggregate should be a performance type, expressed in terms of desired characteristics for the final product. Specifications are primarily based on experience with particular fly ashes since some fly ash may not comply with a given specification for producing an acceptable product.

The economy of using fly ash depends almost entirely on its quality, generation, location, and cost relative to cement, although there may be economic advantages from reduced pouring and finishing time compared to standard concrete. Significant savings in using fly ash can result when large quantities of concrete are involved.

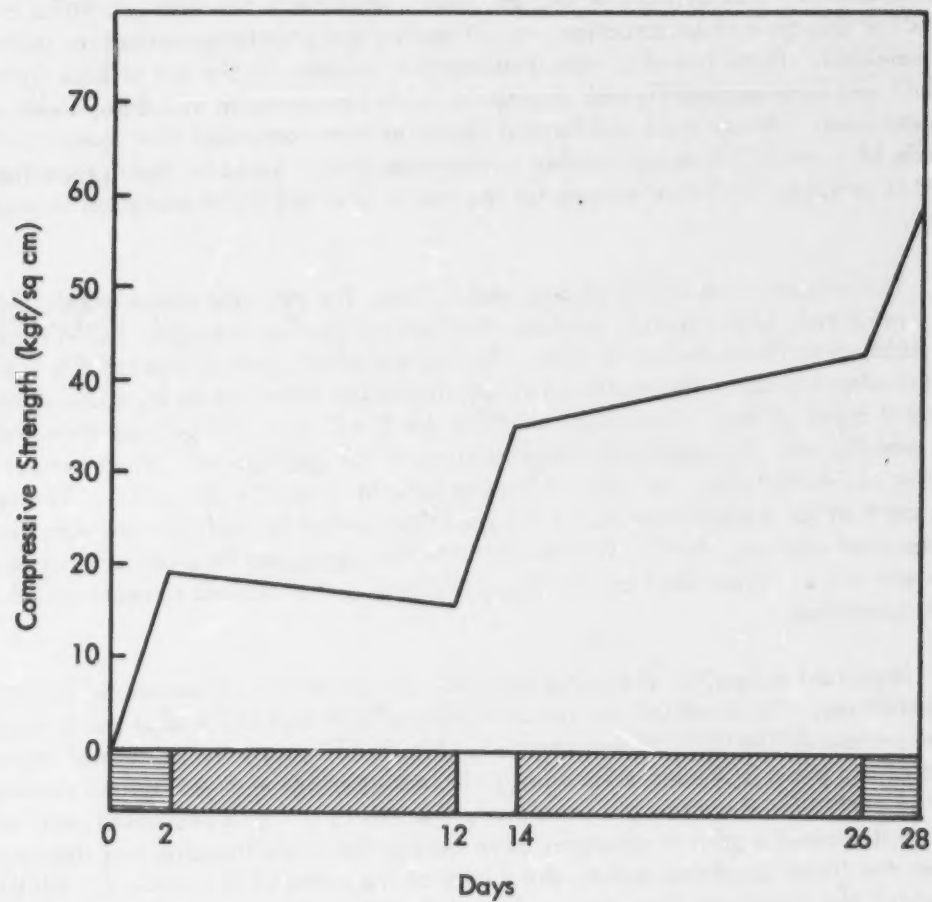
There are some materials handling problems associated with the use of fly ash in concrete. Low viscosity, for instance, may cause problems in feeding and weighing, and the extreme fineness of fly ash can lead to air pollution and other problems, such as poor insulating properties of concrete used in electrical boxes and switches. Proper design of feeders and scales and the installation of dust-collecting systems can eliminate these problems.

Stabilized Bed Construction.

The use of granular material in base and sub-base construction for road and airfield pavements runs into billions of kkg per year. Because of the vast quantities of materials used for this type of construction, an attractive and promising method for utilizing fly ash is provided. There has also been a substantial increase in the use of lime fly-ash aggregate (LFA) and lime-cement fly-ash aggregate (LCFA) mixtures in pavement construction during recent years. Many state and federal agencies have expanded their specifications to include LFA and LCFA as acceptable paving materials. Based on their properties, great potential markets can be developed for the use of LFA and LCFA materials in paving construction.

LFA mixtures are blends of aggregate, lime, fly ash, and water which, when compacted to a relatively high density, produce hard surface paving materials; LCFA contains concrete in addition to the materials in LFA. Aggregates which can be successfully used in LFA and LCFA mixtures cover the entire spectrum, including sands, gravels, crushed stones, and several types of slag. Typical proportions are 2-1/2 to 3-1/2 percent lime and 10 to 25 percent fly ash, depending on the gradations of the aggregates. When cement is used in the LCFA mixtures, the ratio of lime to cement is usually 3:1 or 4:1. The optimum fly ash content for a particular mix is the quantity needed to achieve maximum density in the compacted mixture, that is, fill the voids in the aggregate lime content. The optimum content can be established by trial batch procedures for desired strength and durability characteristics.

Important properties of paving materials are durability, dimensional stability, strength, and stiffness. The standard test for durability of LFA and LCFA mixtures is the cyclic freeze-thaw ASTM C593 designated test. Figure 177 shows the pattern of strength loss and gain of a typical LCFA material during alternate periods of freezing and thawing. As the curing period for the materials increased, the loss in strength decreased until ultimately the material showed a gain in strength, even during the cycle freezing and thawing period. When the latter condition exists, durability of the material is improved. All paving materials in which the aggregate particles are bound together with binders such as cement, asphalt, or lime fly-ash change dimensions with temperature and moisture conditions. Good pavement performance requires that the coefficients of linear thermal expansion of the layers be limited to less than 10^{-5} . If large dimensional changes occur, the pavement will crack excessively, permitting the infiltration of water and foreign material into the pavement with a concomitant failure in pavement performance. Dimensional changes of a typical LFA material under varying moisture and temperature conditions are shown in Figure 178. As a general rule, the coefficients of linear thermal expansion for hardened LFA and LCFA materials can be taken as 5×10^{-6} , or about the same as portland cement concrete.

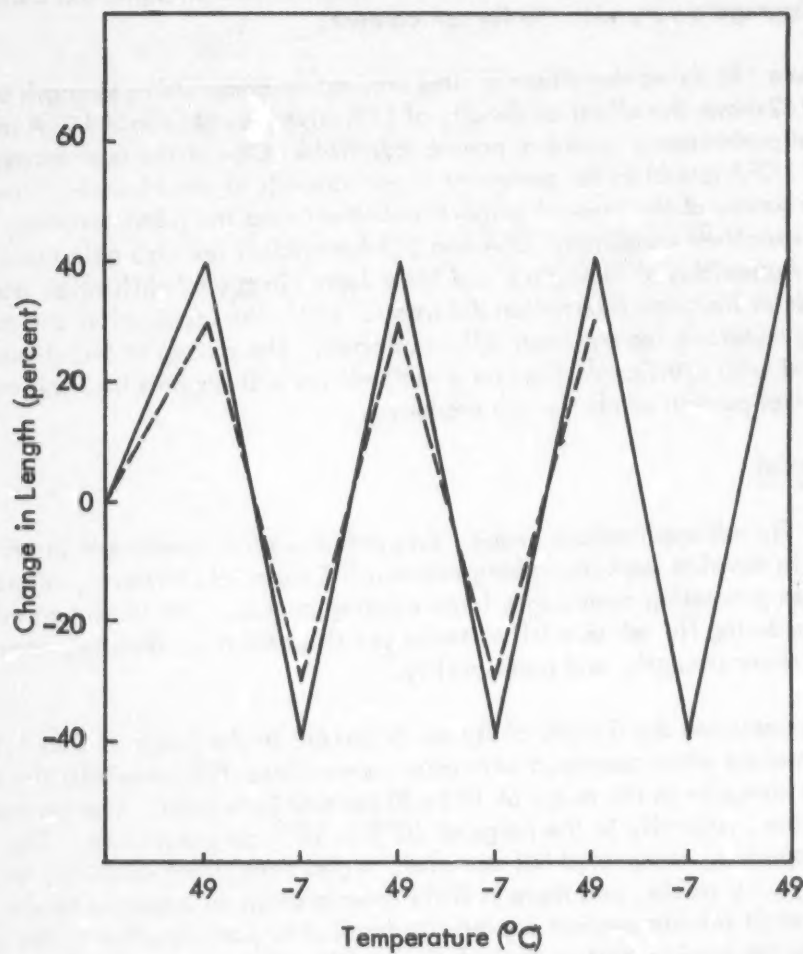


Legend

-  Period of constant 49°C temperature
-  Period of ten freeze-thaw cycles

Source: 23

Figure 177. Effect of freeze-thaw cycles on LCFA compressive strength.



Legend

- Saturated specimens; $\epsilon_t = 8.0 \times 10^{-6}$
- - - Unsaturated specimens; $\epsilon_t = 5.8 \times 10^{-6}$

Source: 23.

Figure 178. Change of length with temperature for cured LFA specimen.

The higher the compressive strength, the better the quality of the LFA mixture. The strength of LFA and LCFA are time and temperature dependent. Some time and temperature versus strength relationships for typical LFA and LCFA mixtures are shown in Figures 179 and 180, respectively. Data in Table 61 shows how the strength and durability of the well-graded aggregate vary with the fly ash content.

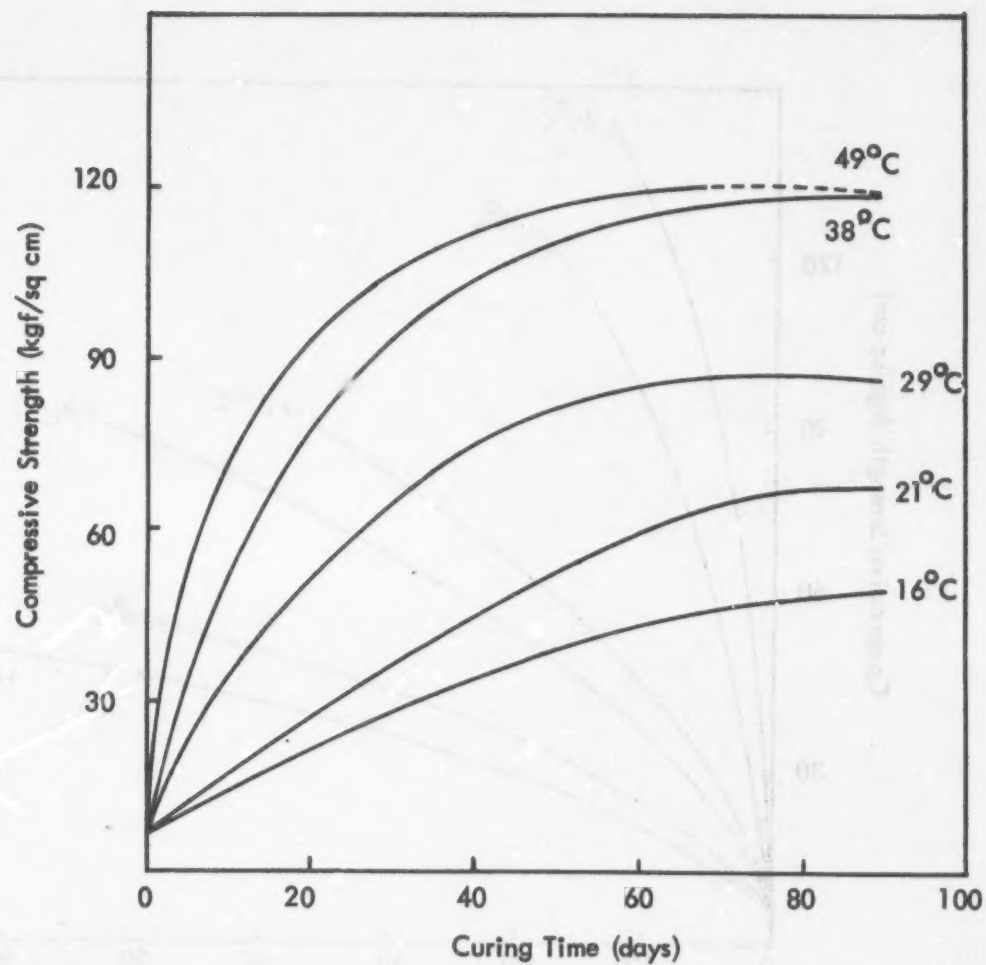
Figure 181 shows the effect of lime content on compressive strength of LFA mixtures; Figure 182 shows the effect on density of LFA mixtures. LCF and LCFA mixtures have an excellent performance record as paving materials. One of the best examples of the use of LFA and LCFA materials for pavement construction is at the Newark, New Jersey airport. A recent survey of the Newark airport facilities found the primary runway and taxiway system to be in excellent condition. LFA and LCFA materials are also being used extensively by the Port Authorities of New York and New Jersey in the rehabilitation and upgrading of the pavements at Kennedy International Airport. Still, the application and marketing of fly ash as paving materials has not been fully exploited. The paving material market is tremendously large, and with additional effort on a national level it appears that this market could absorb a substantial portion of all fly ash produced.

Fill Material

Most fly ash applications require substantial capital investment in processing equipment, and time to develop markets. Using ash as a fill material, however, offers the advantage of minimum processing costs and a large existing market. The important material properties when considering fly ash as a fill material are its grain size, density, compaction characteristics, shear strength, and permeability.

The compacted dry density of fly ash is usually in the range of 1 to 1.5 g/cu cm, which is a high weight when compared with most conventional fill materials; the optimum moisture content is normally in the range of 18 to 30 percent by weight. The permeability of compacted fly ash is low, typically in the range of 10^{-3} to 10^{-5} cm per minute. This is quite adequate for a homogeneous, compacted fill material. Apart from slight solubility in water, fly ash is chemically very stable, and there is little deterioration on exposure to the atmosphere. Also, since the small soluble content is partially fixed after participation in the pozzolanic action, leachate water passing over or through fly ash fill will pick up somewhat lower quantities of soluble chemicals. Strength characteristics are enhanced by the pozzolanic action, and there is a gradual increase of strength with time, as with portland cement.

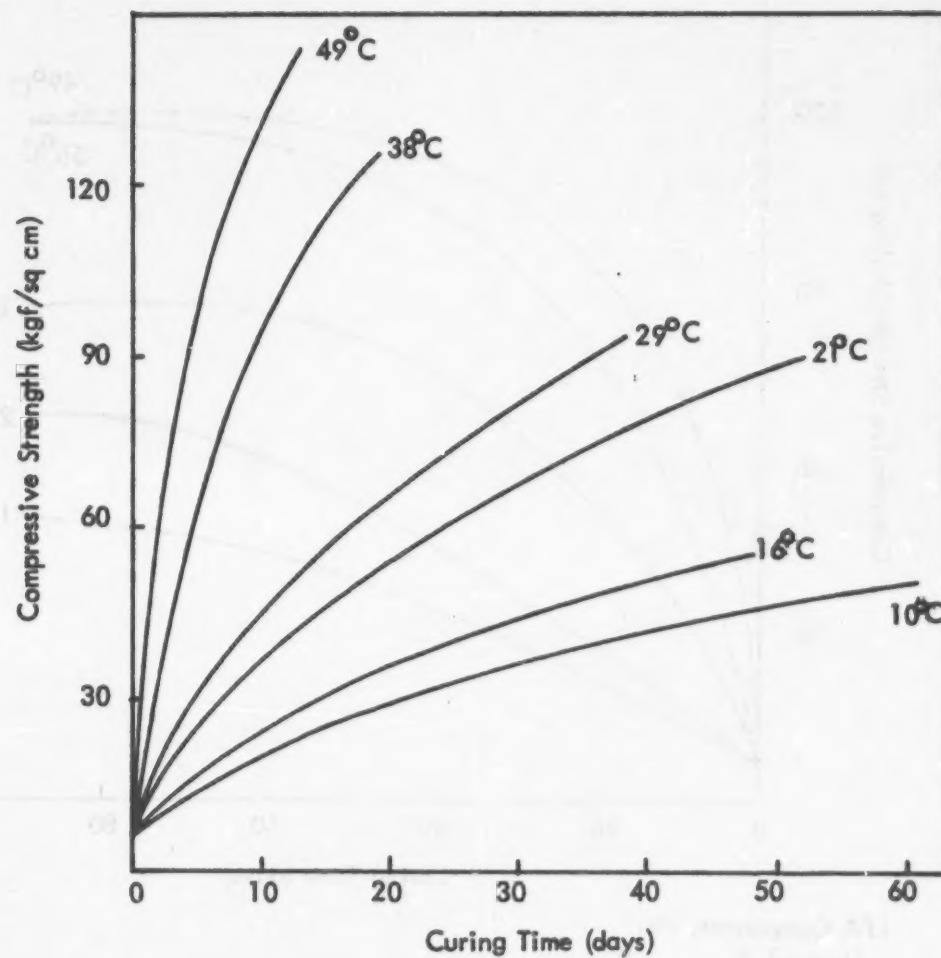
Fly ash's low unit weight and low compressibility help to reduce differential settlement between the approach embankment and the structure itself. Fly ash has also been used as structural fill to retain slurry at Grossblidergtroff Station of the Houilleres du Bassin Lorraine (HBL) in eastern France. Fly ash fill dams were constructed in the valley and the area behind them was then filled with water from a small tributary stream of the Saar river. Waste ash from the generating station was later filled to reclaim land.



LFA Components (%)
 Lime--2.5
 Fly Ash--10
 Aggregate--87.5

Source: 23.

Figure 179. Effect of curing time and temperature on LFA compressive strength.



Source: 23.

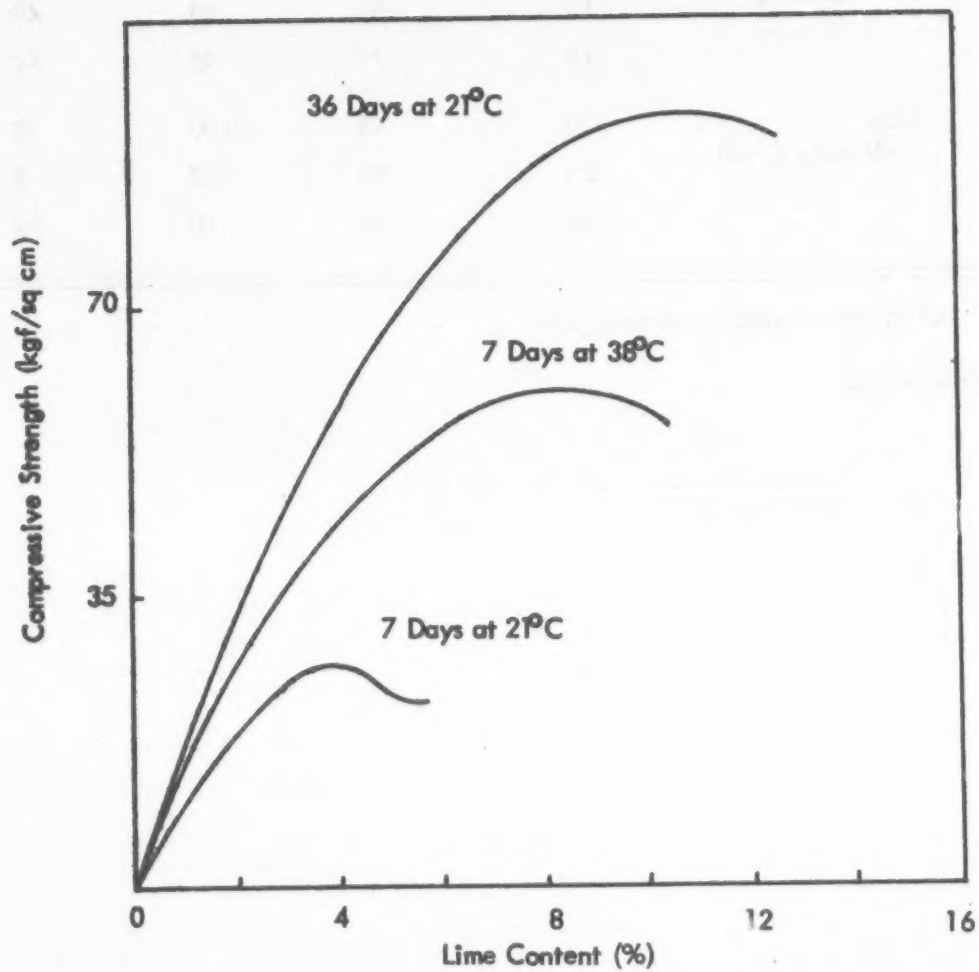
Figure 180. Effect of curing time and temperature on LCFA compressive strength.

TABLE 61. EFFECT OF FLY ASH CONTENT ON LFA STRENGTH AND DURABILITY

Aggregate Type	Fly Ash Content (%)	Compressive Strength (kgf/sq cm)	Durability	
			Weight Loss (%)	Compressive Strength (kgf/sq cm)
Crushed stone (well graded)	10	33	100	0
	12	56	23	49
	15	79	45	69
Slag (uniformly sized)	20	46	100	0
	24	54	58	3
	28	61	10	58

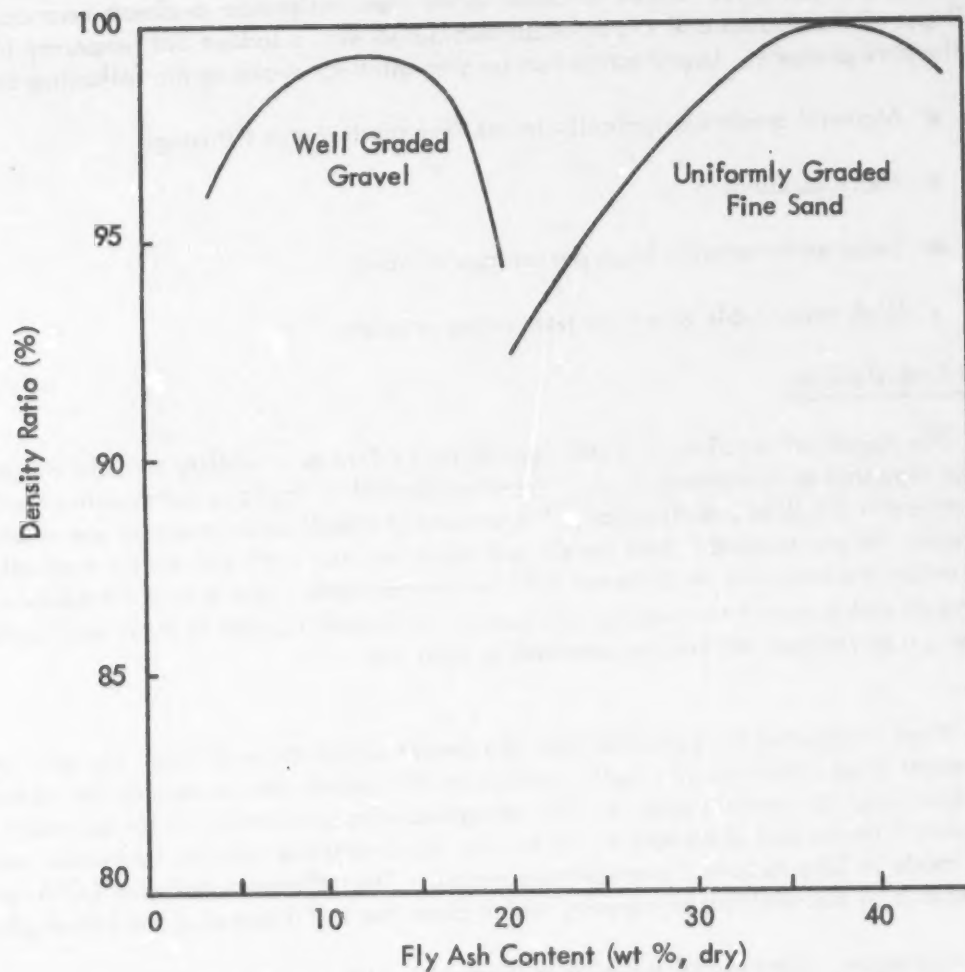
^a All samples contain 3 percent lime.

Source: 23.



Source: 23.

Figure 181. Effect of lime content and curing conditions on LFA strength.



$$\text{Density ratio} = \frac{\text{Density of mixture}}{\text{Maximum density}}$$

Source: 23.

Figure 182. Effect of fly ash content on LFA density.

The major risks with compacted fly-ash fills are ash erosion (both internally and externally) and liquefaction. Internal erosion can be controlled by a properly designed drainage and filter system to ensure that fine material is not carried out of the dam as a suspension in seepage water. External erosion due to wind, rain, and wave action can be controlled by suitable cover vegetation on the downstream slope and slope protection on the upstream slope.

Liquefaction is the sudden decrease in the shear resistance to almost zero caused by collapse of the structure of the material associated with a sudden but temporary increase in the pore pressure. Liquefaction can be prevented by avoiding the following conditions:

- Material gradation typically in the fine sand/coarse silt range
- Shock loadings
- Loose material with large percentage of voids
- High water table or excess pore water pressure

Soil Stabilization

The degree of stability in a soil (wet or dry) refers to its ability to resist deformation under repeated or continuing loads. Treating the soil to improve deformation resistance and strength is called stabilization.³⁴ A variety of stabilization methods are available; however, no one method is best for all soil types because each soil differs markedly in its properties and reactions to different stabilization methods. LFA and LCFA mixtures are two materials which have been successfully used for soil stabilization in many applications, and there is a developed technology concerning their use.

When compacted to high densities, the proper combination of lime, fly ash, aggregate and water dries into a stable, hard, continuous slab which can be used as the subbase or base for bituminous or concrete paving. The amorphous glassy materials in fly ash react to form complex silicates and aluminate which in turn react with the calcium hydroxide and magnesium oxide in lime to form a cementitious matrix. The difference between LCFA and LFA mixtures is in the addition of cement, which gives the LCFA material more strength.

Aggregate. The type of material to be stabilized is an important parameter in LFA/LCFA design. For this purpose, five categories can be identified: clays, silty soils, sandy soils, coarse granular soils, and other fill (pozzolanic materials). Treatment of clays depends greatly on the chemical composition and particle size of the material. The sodium-calcium ion balance is an important factor affecting pozzolanic strength. In practice, ratios of 5-9 percent lime and 10-25 percent fly ash are used in clay soils.

Silty soils composed of less than 10-12 percent clay can be stabilized with lime alone, or with a lime/fly ash ratio of about 1:2. Silty soils containing greater amounts of clay require larger percentages of fly ash.

Sandy soils almost always need the addition of fly ash to promote stabilization because of their coarseness. Sandy soils containing silt and clay (10-30 percent) may be stabilized by lime alone if the clay is sufficiently pozzolan. However, addition of fly ash will produce better results. Lime-fly ash ratio of 1:5 are common for sandy soils alone, but gradation will improve strength and durability.

Coarse soils generally need little (2-4 percent) or no lime to meet stability requirements for base courses. The strength of mixes containing clay or caliche can be further enhanced by the addition of fly ash (lime/fly ash ratios of 1:5 are appropriate). Materials such as scoria, cinders, chert, or water-cooled slag have been used in LFA/LCFA compositions with strengths approaching that of portland cement being reported. Fly ash not only contributes to the natural pozzolanic qualities of the above mixtures, but also improves the gradation which results in greater strength.

Lime. Dolomite limes (quicklime and monohydrate) result in 30 percent stronger products than calcitic limes, except in kaolinitic material where the strengths are about the same. Currently, it is believed that the MgO in dolomitic limes acts as a catalyst in the soil-lime reaction. Calcium to mg ratios of 1:1 and 2:1 are optimal (magnesium must be in the oxidized state), and most commercial dolomitic monohydrate limes are within these limits. No optimum ratio of lime to fly ash has been found which satisfactorily stabilizes all soils. As the lime to fly ash ratio is not very critical, and lime is 5 to 10 times more costly than fly ash, it is desirable to use mixtures which maximize the percentage of fly ash.

Moisture. To obtain maximum strength in the hardened product the moisture content of the LFA/LCFA mixture must be near optimum. Optimum moisture content varies depending on the lime/fly ash ratio. In general, the moisture content which results in the maximum bulk density of the lime-fly ash mixture is slightly higher than that needed for the maximum hardened strength. The carbon content and fineness of the fly ash, as well as the flocculating effects of the lime, all affect moisture content. Determining the optimum moisture content for a particular mix of lime, fly ash, and aggregate can be facilitated by preparing a figure similar to Figure 183. In this case, limits of 50:50 soil-lime, 50:50 soil-fly ash, and 100 percent aggregate were selected. Laboratory analysis determined the optimum moisture concentrations for these limits to be 29.2, 17.9/ and 16.7, respectively. Intermediate moisture concentrations are scaled off as shown from 18 to 28 percent. The approximate optimum moisture content can then be read for any soil mix within the original limits.

There are two questions which remain to be answered with respect to fluidized-bed residues in LFA and LCFA soil stabilization mixtures. First, do they work as well as conventional fly ash? Second, because of the limestone content and the pozzolanic action of the residues, can some of the lime and/or cement be replaced by the fluidized-bed residues? Work is in progress to answer these questions.

Neutralization of Acid Mine Drainage

Acid mine drainage (AMD) annually causes millions of dollars of environmental damage. Polluted water taken by downstream users for industrial, agricultural, or potable

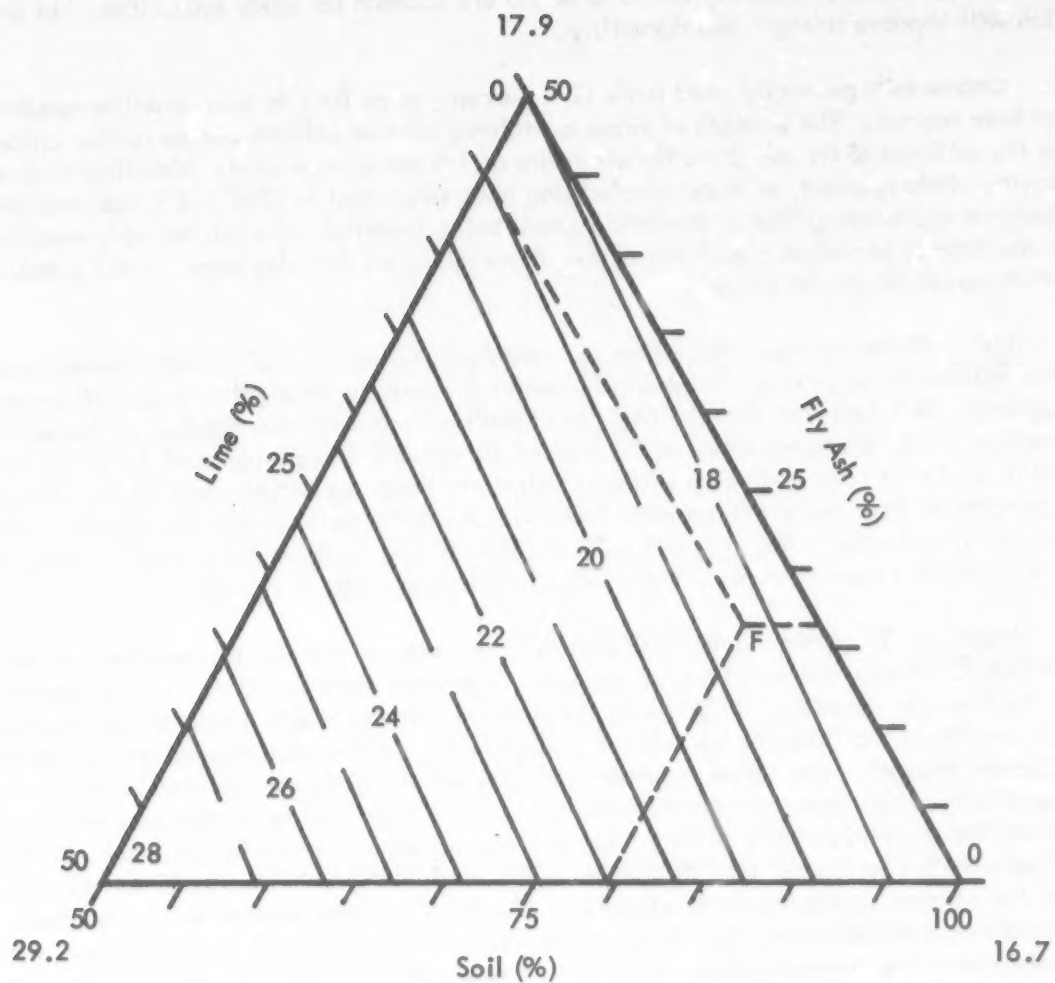


Figure 183. LFA moisture correlation chart.

applications may require additional pretreatment; fish and vegetation may be killed, agricultural land damaged, and an area's recreational value reduced. The problem arises when mining activities expose pyrites and marcasites to the oxygen in the air. In the presence of moist air, sulfuric acid is formed. Every kg of iron sulfide exposed has the potential to produce as much as 1.6 kg of sulfuric acid. The extent of the pollution damage depends on how much sulfide oxidation has occurred and how much acid has been released into the environment.

There are two basic approaches to dealing with AMD: prevent its formation or prevent it from contaminating ground or surface waters. One approach which has been tried experimentally is to collect the acid as it forms and pump it to storage and treatment facilities, where it is neutralized with lime or other chemicals before discharge. This is an expensive alternative, especially if taken to its ultimate end of a treatment plant for every coal mine, operating or abandoned. Since the formation of acid is initiated by oxygen, attempts have been made to prevent contact between the sulfides and air or water. Mines have been sealed to prevent water infiltration or exclude air, but results have not been promising.

Work has been done with using conventional coal fly ash residues for reclamation of surface-mine spoils.³⁴ The residues provided nutrients needed by the soil, served as a conditioner, and their alkalinity has reduced the AMD. Our preliminary analysis suggests that fluidized-bed residues could be used to neutralize AMD, both from strip and subsurface mines. Neutralization capacity varies widely with the type of residue (see Figure 184). Potential use for AMD control will therefore depend partially on the characteristics of the specific residues available.

The marketing potential of fluidized-bed residues for AMD is difficult to determine. Residues used in this way are not directly part of the mining production process. If this application proves feasible, the demand for residues would depend primarily on environmental regulations--the more restrictions placed on AMD and the more stringent the requirements on strip-mine reclamation, the higher the demand. Power producers must, as part of their normal production process, dispose of the residues generated. They will dispose of them by the least expensive means. The assumption of a zero f.o.b. price at the power plant for the residues would not be likely to hold for AMD application. The large quantities of residues required plus their low return to the mine owner suggest that the power plant would need to contribute some or all of the freight charges.

In general, residues would most likely be used for AMD control where the mine site is as close or closer than the landfill site. The mine could be expected to pay the cost of spreading the residues and perhaps some of the transport costs, and special environmental protection measures and other costs would likely be incurred by a landfill operator, but not by the mine operator. Thus, it is likely that fluidized-bed residues could be economically shipped somewhat farther for AMD neutralization than for landfilling.

The market potential for fluidized-bed residues will thus be primarily determined, assuming the application is technically feasible and there are significant regulations concerning AMD, by the location of mine sites relative to power plants. Residues from

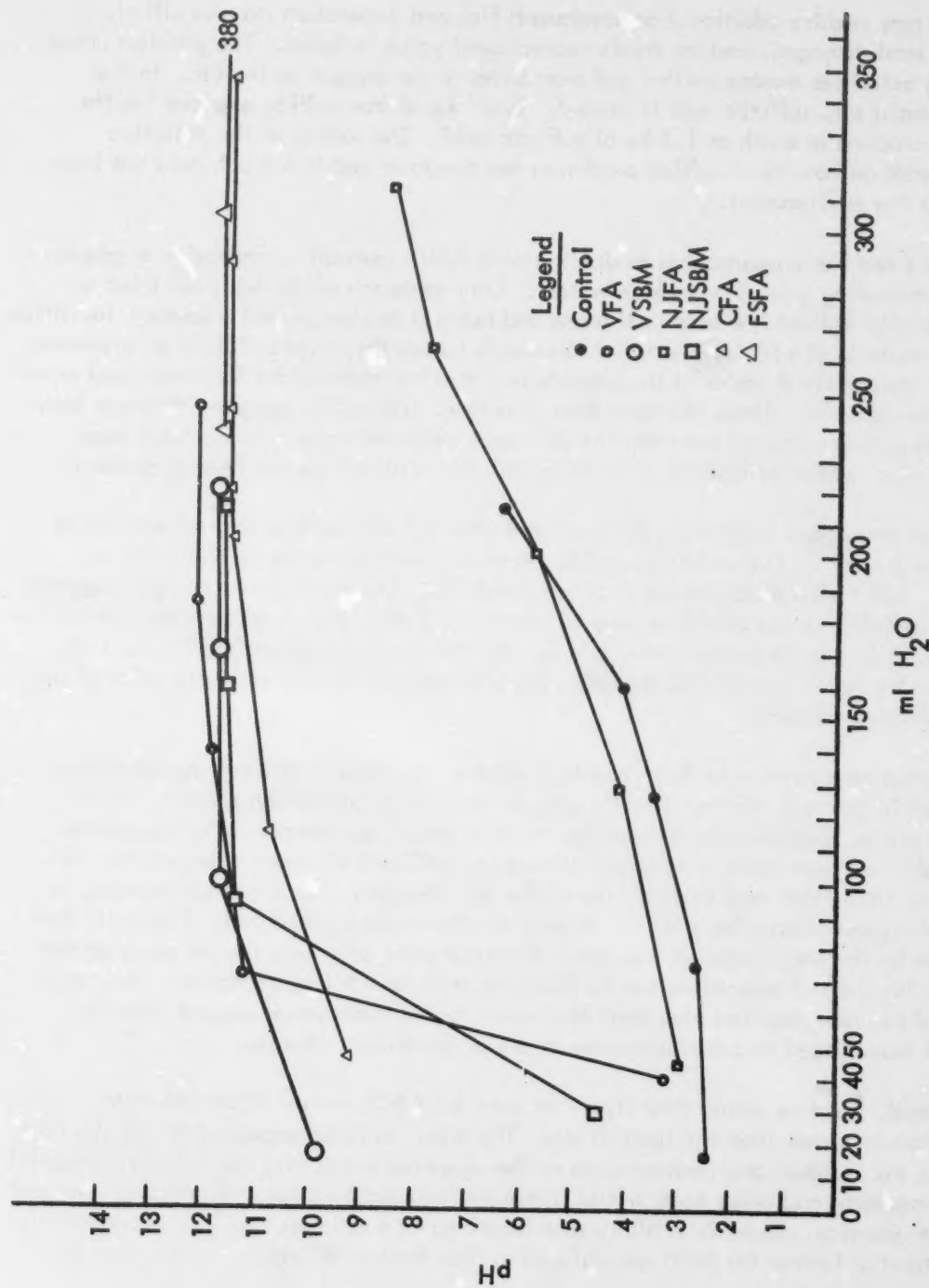


Figure 184. pH of leachate for acid mine drainage control.

coal-burning plants will, at present, tend to be available only for eastern United States mines, as most coal-fired power plants are now located in the East. There are several areas in the East where power plants and mining areas are in particularly close proximity. If fluidized-bed oil gasification becomes widely adopted, many more mining areas will have a nearby source of residues.

Soil Cement

Soil cement is a mixture of soil, portland cement, and water. Compacted at optimum moisture content and cured to hydrate the cement, soil cement forms a strong stable base that is resistant to variations in moisture and temperature. Soil cements typically have modules of elasticities which range from 100,000 (for clayey soils with little cement) up to 10^6 (for stronger mixtures), and are far more elastic than concrete. Soil cement mixtures are used for base courses under pavement, roadway shoulders, patching, ditch and channel linings, dam facings, and miscellaneous uses.

In general, there are three types of soil cement: compacted soil cement, cement modified soil, and plastic soil cement. Compacted soil cement contains the stoichiometric amount of cement to harden the soil and the stoichiometric amount of water to hydrate the cement. Cement-modified soil is an unhardened or partially hardened mixture of soil and cement. Just enough cement and water are added to the soil to change its chemical and physical properties. Addition of cement to soil reduces the soil's plasticity and water holding capacity, and increases its bearing value. Plastic soil cement contains sufficient water, at the time of placing, to give the mix a consistency similar to that of plastering mortar.

The surface of a cured soil cement mixture is friable, hence it cannot be used as a running surface for motor vehicles without experiencing scuffing and pitting. It is usually overlaid with a layer of bituminous or concrete paving, the type of covering determining to some extent the type and thickness of the soil cement sub-base.

Soil cement is an inexpensive paving material because of the three basic materials needed. Soil and water are either found at the site or transported only short distances. The word "soil" as used in "soil cement" means any combination of gravel, sand, silt, clay, or filler (such as cinders, shale, chat, etc.). The water used in soil cement preparation serves two purposes: it aids in compaction by lubricating soil grains, and it is necessary for cement hydration.

Soil gradation is an important factor in proper soil cement design. Sandy and gravelly soils with about 10-35 percent silt and clay combined are the most desirable soil cement aggregates and generally require the least amount of cement for satisfactory curing. Coarse soils containing 55 percent or more material passing the number four sieve also make good soil cement aggregates. Sandy soils deficient in fines can make adequate soil cement, although the amount of cement needed increases as the percentage of fines decreases. Silty and clayey soils also can be used to make satisfactory soil cement; however, the higher the clay content, the greater the amount of cement needed to provide adequate hardening.

Silty and clayey soils are sensitive to weather conditions (much more so than coarse or well graded soils).

The amount of portland cement needed to construct a suitable soil cement pavement depends on soil type and design load. Any type of portland cement which complies with ASTM or AASHTO specifications is satisfactory. Types 1 and 1A, normal and air-entraining portland cements are most commonly used. Tables 62 and 63 show representative cement concentrations for various soil types.

When possible, the optimum amount of moisture to add to a soil cement mixture should be determined by a laboratory test, such as AASHTO T134 "Standard Method of Test for Moisture-Density Relations of Soil-Cement Mixtures." In general, sandy mixtures will require approximately 22 l of water per sq m for a 15-cm compacted thickness. Silty and clayey mixtures will require about 32 l of water per sq m. Experienced users can, within practical limits, determine the optimum moisture content by test. Soil cement at optimum moisture contains sufficient water to form a firm cast; when squeezed in the hand, water cannot be squeezed out.

In practice, soil cement is generally mixed in-situ or less commonly away from the construction site and then trucked in. In-place mixing is more economical; off-site mixing is used only when the quantity or quality of the aggregate at the site is not adequate enough to meet the design standards. Mixing of the aggregate and cement can be either on the ground (continuous mixing) or in a mixer (either traveling or stationary). Mixers provide a better control over the amount and blending of the components. Groundmixing is cheaper and usually faster; it can be done using a dump truck or even by hand. Compaction is usually done by rollers; however, in sandy soils or coarse soils lacking in fines, compaction must be done by vibration.

Curing soil cement mixtures have to be protected from the weather in order to prevent moisture imbalance. Bituminous coatings are generally used, but dirt, straw, and paper have all been successfully applied.

Agriculture and Reclamation

Residues can be used to eliminate acid type agricultural soils. Soil pH is also an important factor in determining the solubility of many compounds such as the concentration of heavy metals present in crops. It had been observed that in a strongly acid soil, large amounts of metals such as iron, aluminum, and manganese may come into solution and may be adsorbed on the surface of the soil particle. Plants can easily take up metals in this form.¹⁹¹ Soil with a safe toxic metal content at pH 7 can easily be lethal to most crops at pH 5.5. However, it has also been found that an increase in pH will decrease the plant uptake of heavy metals. Application of sewage sludge or effluent irrigation may generally tend to lower the soil pH, and the addition of calcareous or magnesium compounds to soil can correct or eliminate acidic soil conditions.

TABLE 62. AVERAGE CEMENT REQUIREMENTS OF MISCELLANEOUS MATERIALS

Material	Percent by Volume	Percent by Weight
Caliche	8	7
Chat	8	7
Chert	9	8
Cinders	8	8
Limestone screenings	7	5
Marl	11	11
Red dog	9	8
Scoria containing plus No. 4 material	12	11
Scoria (minus No. 4 material only)	8	7
Shale or disintegrated shale	11	10
Shell soils	8	7
Slag (air-cooled)	9	7
Slag (water-cooled)	10	12

Source: 189.

TABLE 63. NORMAL RANGE OF CEMENT REQUIREMENTS FOR B AND C HORIZON SOILS^a

AASHTO Soil Group	Percent by Volume	Percent by Weight
A-1-a	5-7	3-5
A-1-b	7-9	5-8
A-2-4, A-2-5, A-2-6, A-2-7	7-10	5-9
A-3	8-12	7-11
A-4	8-12	7-12
A-5	8-12	8-13
A-6	10-14	9-15
A-7	10-14	10-16

^a "A" horizon soils may contain organic or other material detrimental to cement reaction and may require higher cement factors. For dark grey to grey A horizon soils, increase the above cement contents four percentage points; for black A horizon soils, six percentage points.

Source: 189.

Related information on the effects of zinc level and soil pH on chard plants are shown in Table 64. Inorganic zinc (and cadmium at one percent of the added zinc) was added to a sassafras sandy loam soil and the pH was adjusted to 5.3, 6.4, or 7.2 in the metal amended soil. The concentration of zinc uptake in plants may be significantly reduced when the soil pH is increased by the addition of lime or other pertinent alkaline materials. (A brief literature search identified previously published data and conclusions showing the same trace metal uptake improvement).¹⁹¹

Addition of sulfur will reduce the soil pH. The reduction of soil pH is directly proportional to the quantity of sulfur added. Lowering the soil pH increased the concentration of metals as shown in Table 65 and certain other elements such as silicon, phosphorus and potassium.

At the Virginia Polytechnical Institute, other field research on using fly ash as a fertilizer is seeking to determine (1) the plant nutrients available in fly ash and (2) the effects of different fly ash application rates. Research on revegetating several barren experimental sites has proven that fly ash could act as a neutralizing agent, diluent, and soil conditioner to provide needed nutrients which enhance vegetation growth.⁸⁴

The U.S. Park Service, Washington, D.C., is testing sintered fly ash for use as an additive to soils subjected to continuous use (bicycle paths, camping areas, hiking trails, picnic areas). In this application, sintered fly ash would be added for its porosity and resistance to degradation.

Brick Manufacture.

Using fly ash as an additive can extend the life of a clay or shale deposit; this is of particular value to brick plants with limited raw materials supplies. Extensive research on fly ash in brick has been done at the Coal Research Bureau of West Virginia University. This research has yielded tolerance levels for many fly ash constituents which, when exceeded, contribute to a poor quality brick. These constituents include: water soluble minerals, water soluble sulfur, carbon, iron, and alkaline earths. The first commercial fly ash brick plant using the process developed at the Coal Research Bureau is operating at Edmonton, Alberta. The plant has a design capacity of 35 million bricks per year. Economic studies currently underway indicate that the cost of the Coal Research Bureau process is less than that of the conventional clay-brick manufacturing process. Several firms are currently examining the process for commercial exploitation. Research is underway on coloring and texturing the brick, and on producing large size bricks.

Water Quality Improvement.

Fly ash as a treatment material for reclaiming small eutrophic or algae-overgrown lakes is under study at Notre Dame University. Fly ash can remove phosphates in the water and seal the bottom mud so that the release of pollutants is controlled. A process for the removal of phosphates from water using fly ash has been developed at the Polytechnic Institute, Brooklyn, N.Y. When used for water treatment, fly ash will (1) increase

TABLE 64. EFFECTS OF ADDING Zn AND VARYING THE pH
IN THE SOIL ON Zn CONTENT AND YIELD REDUCTION
OF CHARD LEAVES

Added Zn ppm	Soil pH ^b		
	5.3	6.4	7.2
1.31	210	116	12
32.7	754	237	74
65.4	1058(7) ^a	337(5)	100
131.0	2763(41)	765(9)	177
262.0	2692(95)	1678(22)	406(27)

^aYield reduction in parentheses (%).

^bg. Zn/g dry weight.

Source: 191.

TABLE 65. EFFECTS OF SOIL pH ON SOYBEAN PLANT'S MINERAL UPTAKE

Elements in ppm	Soil pH		% Increase	Elements yield	
	7.4 ^a	6.1 ^b		7.4 ^a	6.2 ^b
Fe	31	81	261.2	5.6	18.5
Mn	47	209	444.6	8.5	47.7
Zn	40	68	170.0	1.72	2.87
Co	6.6	12.3	186.3		
Mo	9.5	12.6	132.6		
Al	9.6	16.4	170.8		
B	72	123.0	170.8		
Ni	4.4	7.7	175.0		
Si	2000	3800	190.0		
P	4300	6500	151.1		
K	17,300	25,900	149.7		

^aNo sulfur added.

^b10% sulfur added.

^cP154619-5-1 soybean variety.

Source: 192.

the growth of flocs, thus enhance settling, (2) condition the waste sludge as a physical aid to filtration, (3) remove phosphates, and (4) absorb organic molecules in solution.

Miscellaneous.

Industrial applications for the hollow, spherical, and extremely light-weight fly ash particles known as cenospheres are being developed at Washington State University. One application, known as "syntactic foam," is used to achieve buoyancy in deep ocean environments. Syntactic foam is formed by vacuum impregnating cenospheres with an appropriate resin. Research on aerospace applications of cenospheres is underway at the Grumman Aerospace Corporation. From this research, a closed pore insulation material for use on the space shuttle has been developed. A unique application using cenospheres in the production of a tape for fire proofing and insulating high-voltage electrical cable has been developed by the Quelcor Corporation.

Specific Applications of Lime/Limestone Wet Scrubber Residues

"Modified fly ash," the solid by-product from lime/limestone wet-scrubbing, is a new solid waste material which has different chemical and physical properties from regular fly ash. Modified fly ash has little potential for mineral separation and beneficiation, and therefore, must be used in its homogeneous state. The Coal Research Bureau has developed several promising uses for modified fly ash. Several potential applications are considered below:

- Soil amendment
- Highway construction
- Aerated concrete
- Poured concrete

Soil Amendments.

Dried modified fly ash can be used as a soil amendment to increase the calcareous component, and to neutralize acid soil. Modified fly ash may also increase the concentrations of boron and other trace elements, and also increase the texture and drainage characteristics of soils. Further research is needed to determine if pollution would be created by water leaching.

Highway Construction.

Combustion Engineering participated in a project with the Research and Development Division of the Federal Highway Department to study the use of residues as a highway construction material. The program was part of the International Transportation Exposition (Transpo '72) that was held from May 24 to June 4, 1972 at the Dulles Airport in Washington, D.C. To accommodate the 50,000 automobiles and 600 buses arriving daily at the

exposition, a 49 hectare parking lot was constructed. The Research and Development Division of the Federal Highway Administration used this opportunity to demonstrate the recycling of waste products as highway construction materials. The major portion of the parking lot was paved with a mixture of modified fly ash and sulfate sludge from an acid plant.

Aerated Concrete.

Aerated concrete has been widely developed in Europe. Almost all new factory buildings in Sweden and West Germany are constructed, in part, using this material. Aerated concrete is a light-weight structural material consisting of small non-communicating gas cells entrained in a calcium silicate matrix. A process flow sheet for the production of aerated or foamed cellular concrete from modified ash is shown in Figure 185. It is necessary to add cement and a gas-producing agent to modified fly ash in making this product. Commercial aerated concrete varies from 0.3-0.8 g/cu cm in density, and has a compressive strength of about 30-60 kgf/sq cm.

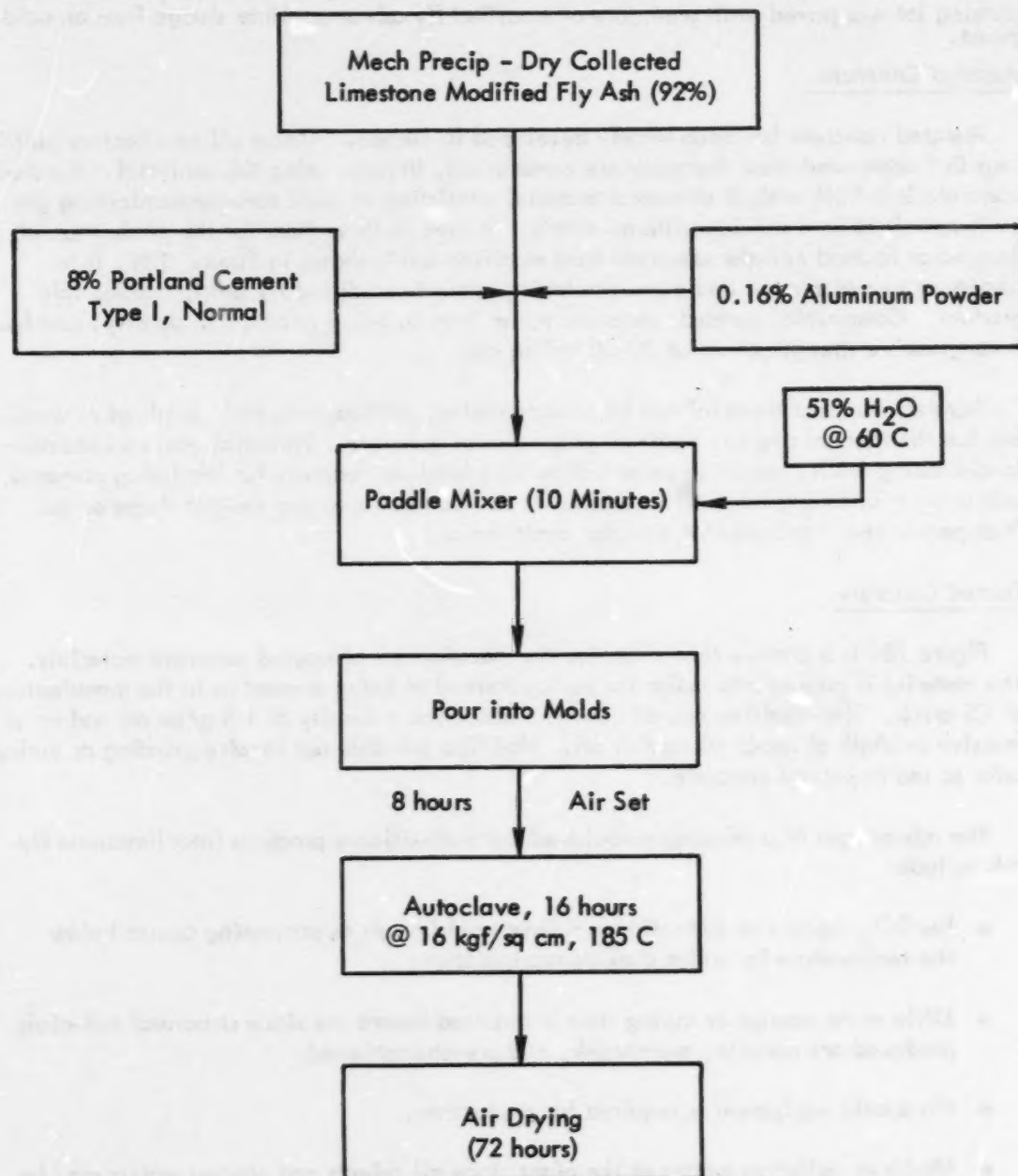
Aerated concrete material can be sawed, nailed, drilled, screwed, or glued as wood, but has the thermal and fire resistant properties of concrete. Potential uses include non-load-bearing walls, sandwich construction with brick or concrete for insulating purposes, and interior surfacing for exterior walls. It can be formed in any desired shape or cut from panels and is suitable for modular construction.

Poured Concrete.

Figure 186 is a process flow sheet for the manufacture of poured concrete materials. The material is poured into molds for curing instead of being pressed as in the manufacture of CS brick. The resulting poured concrete block has a density of 1.5 g/cu cm and compressive strength of about 60 kgf/cu cm. Modified ash does not require grinding or curing prior to use in poured concrete.

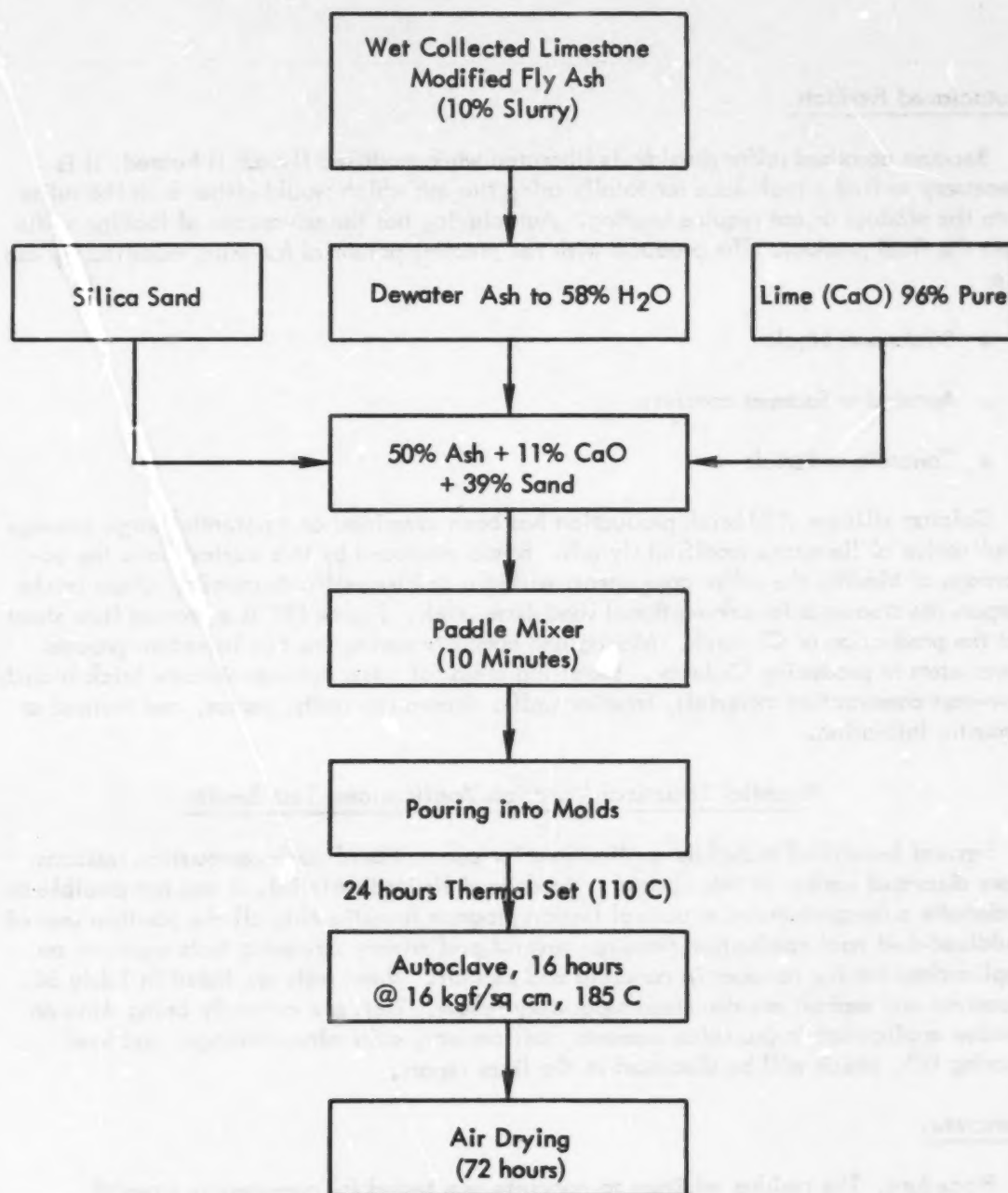
The advantages of producing autoclaved calcium-silicate products from limestone fly ash include:

- No SO₂ capture or marketing problems would result as processing occurs below the temperature for sulfur dioxide regeneration.
- Little or no storage or curing time is required before use since structural materials produced are durable, pre-shrunk, and pre-strengthened.
- No exotic equipment is required for production.
- Minimum pollution occurs at the plant since all rejects and process waters may be recycled.
- A potentially large market exists in low-cost housing or other construction.



Source: 46.

Figure 185. Aerated or foamed cellular concrete production flow diagram.



Source: 46.

Figure 186. Formed concrete production flow sheet.

Autoclaved Products.

Because absorbed sulfur dioxide is liberated when modified fly ash is heated, it is necessary to find a technique for totally using the ash which would either lock the sulfur into the product or not require heating. Autoclaving has the advantage of locking sulfur into the final product. The products with the greatest potential for using modified fly ash are:

- Bricks and blocks
- Aerated or foamed concrete
- Concrete materials

Calcium silicate (CS) brick production has been examined as a potential large tonnage application of limestone modified fly ash. Bricks produced by this method have the advantage of binding the sulfur components within a calcium-silicate matrix. These bricks surpass the standards for conventional sand-lime brick. Figure 187 is a process flow sheet for the production of CS brick. Mixing and humidity curing are two important process parameters in producing CS brick. Promising areas for using calcium silicate brick include low-cost construction materials, interior walls, decorative walls, patios, and thermal or acoustic insulation.

Potential Structural Materials Applications: Test Results

Several beneficial materials applications for conventional coal-combustion residues were discussed earlier in this chapter. Because of limited material, it was not possible to undertake a comprehensive structural testing program investigating all the possible uses of fluidized-bed coal combustion residues; several preliminary screening tests were run on applications for the residues in concrete and asphalt. These tests are listed in Table 66. Concrete and asphalt are discussed separately below. Tests are currently being done on residue application in pozzolan cements, soil cement, acid mine drainage, and load bearing fill, which will be discussed in the final report.

Concrete.

Procedure. The residue addition to concrete was tested for compressive strength. Twenty batches of concrete were mixed, differing in the amount and type of residue added. Two of the twenty were control samples in which no residues were added. Four sample specimen cylinders were made from each batch. The procedure followed for making the cylinders was ASTM C192-69 ("standard method of making and curing concrete test specimens in the laboratory"); the cylinders were approximately 5 cm in diameter by 10 cm in length. Table 67 gives the composition of each batch. The mixtures are considered "rich mixes" because of the high cement content (approximately 15 percent).

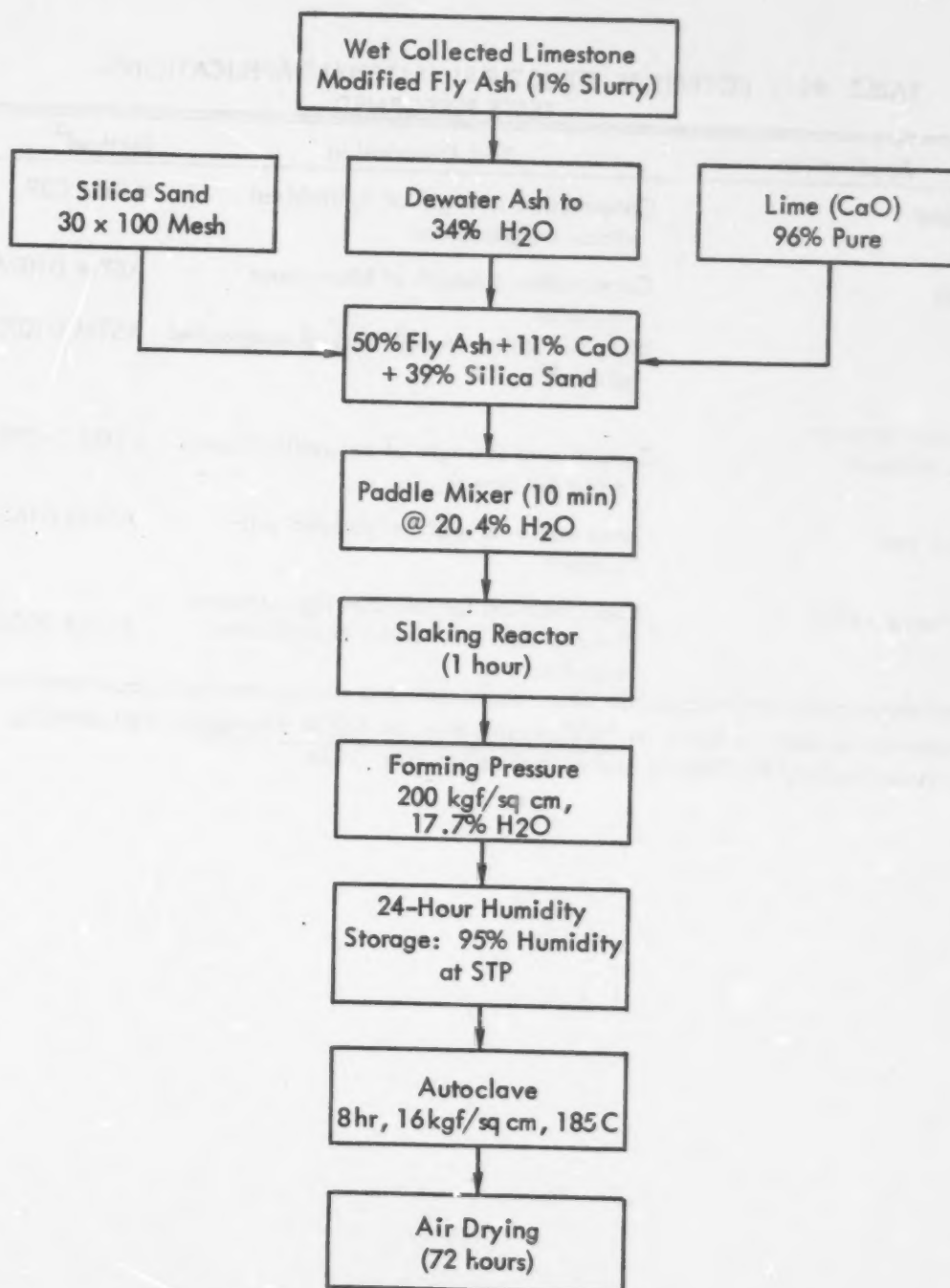


Figure 187. CS brick production flow diagram:

TABLE 66 . POTENTIAL STRUCTURAL MATERIALS APPLICATIONS:
TESTS PERFORMED

Application	Test Description	Method ^a
Concrete	Compressive strength of cylindrical concrete specimens	ASTM C39
Asphalt	Compressive strength of bituminous mixtures	ASTM D1074
	Effect of water on cohesion of compacted mixtures	ASTM D1075
Pozzolan cements LFA mixtures	Compressive strength of cylindrical concrete specimens	ASTM C-593
Soil cement	Compressive strength of molded soil-cement	ASTM D1633
Load-bearing fill	Classification for engineering purposes	—
	Direct shear: soil under consolidated condition	ASTM D3080

^a Reference numbers as found in 1974 Annual Book of ASTM Standards. Philadelphia: American Society for Testing and Materials (ASTM), 1974.

TABLE 67. COMPOSITION OF CONCRETE TEST CYLINDERS

Batch No. ^a	Type of Residue ^b	Concrete Composition (% by weight)			
		Residue	Fine Aggregate	Portland Cement	Water
1	Control	0	71.5	15.2	13.3
2	VSBM	5.2	64.8	14.9	15.1
3		15.8	53.6	14.7	15.9
4		25.0	41.0	14.0	20.0
5	NJFA	5.3	64.7	14.9	15.1
6		15.7	53.4	14.7	16.2
7		25.0	41.0	14.0	20.0
8	VFA	5.2	63.7	14.6	16.5
9		15.0	51.0	14.0	20.0
10		24.7	40.5	13.8	20.9
11	Control	0	71.5	15.2	13.3
12	NJSBM	5.3	64.7	14.9	15.1
13		15.2	53.7	14.7	16.4
14		25.7	43.2	14.7	16.4
15	EFA	5.2	64.8	14.9	15.1
16		15.2	53.7	14.7	16.4
17		25.1	41.0	14.0	20.0
18	ESBM	5.3	64.7	14.9	15.1
19		15.2	53.7	14.7	16.4
20		25.1	41.0	14.0	20.0

^a Two samples for each batch.^b Residue source code presented in Table 6.

One sample from each batch was tested after curing for seven days; another, after twenty-eight days. After curing, the cylindrical molds were removed and the diameter of the cylinders measured to obtain average cross-sectional area; the results are shown in Tables 68 and 69. Each cylinder was then capped to prepare them for the actual compressive strength tests. The results of the tests are presented in Table 70 for the seven day curing and in Table 71 for the twenty-eight day curing.

Results. The results are shown graphically in Figures 188 to 191, which plot compressive strength versus residue strength. In general, the strength increased with curing time for all the fluidized bed residues. The only exception was the concrete containing more than about 18 percent by weight of EFA. This was due to the unique property of the 7 day cured EFA. Like the other residues, the strength of the concrete decreased from 5 to 15 percent residue; however, at 25 percent residue content, the compressive strength had increased to a value higher than the concrete containing 5 percent residue.

Optimum residue percentages varied widely. Strengths increased with increasing residue concentration for fly (7 day cure) and spent bed materials from the Exxon, New Jersey, pressurized miniplant. On the contrary, with the exception of VFA (28 day cure) and the EFA (7 day cure), strengths decreased with increasing content of residues from the PER, Virginia atmospheric pressure unit and from the Esso gasifier. The following concrete test specimens showed unconfined compressive strengths greater than the control specimens: 5 percent VSBM/7 day cure; 5, 15, and 25 percent VSBM/28 day cure; 5, 15, and 25 percent NJFA/28 day cure; and 5 percent VFA/28 day cure. The 25 day NJFA/7 day cure material was nearly equal to the control.

Asphalt

Procedure. Residues were tested as replacements for aggregate filler in asphalt. Samples were made and tested for compressive strength following the procedures outlined in ASTM-D-1074; test cylinders were approximately 10 cm in diameter and length. Residue contents tested were 0, 20, 45, 82, and 92 percent of aggregate volume (measured by weight from specific gravities). The aggregate conformed to State of California Department of Transportation 3/8-inch maximum gradation specifications. To simplify handling and to lower test cost, emulsified asphalt (SS-1H) was used in concentrations of 8 to 13 percent by weight. Compression tests were also performed for samples containing portland cement, lime or hydrochloric acid additives. Table 72 summarizes the sample compositions.

All residues were slaked before being added to the asphalt mixtures. Unslaked residues produced poor results, particularly the Exxon spent bed material. Reactions between the residue and the emulsified asphalt resulted in a significant decrease in density. In some cases, expansion of the residue was enough to completely disintegrate the test specimen which resulted in a crumbly pile of aggregate and partially coated residue (See Figure 192).

Samples were subjected to a compacting load of 17,199 kg for two minutes. Samples were then measured and coded, and those that were within 10.16 ± 0.64 cm in length were cured in an oven at $60 \pm 3^\circ\text{C}$. One sample of each composition was cured for 29 hours and one for 7 days.

TABLE 68 . DIAMETER AND AREA OF CONCRETE TEST CYLINDERS:
SEVEN-DAY CURE

Batch No. ^a	Diameter (cm)				Average Diameter (cm)	Average Cross- sectional Area (sq cm)
	b	b	c	c		
1	5.37	5.77	5.69	5.45	5.57	24.37
2	5.45	5.77	5.85	5.45	5.63	24.89
3	5.61	5.77	5.69	5.69	5.69	25.43
4	5.77	5.77	5.37	5.77	5.67	25.25
5	5.45	5.77	5.77	5.61	5.65	25.07
6	5.37	5.85	5.85	5.37	5.61	24.72
7	5.53	5.69	5.69	5.61	5.63	24.89
8	5.77	5.45	5.45	5.69	5.59	24.54
9	5.77	5.45	5.45	5.77	5.61	24.72
10	5.61	5.53	5.53	5.61	5.57	24.37
11	5.40	5.32	5.40	5.32	5.36	22.56
12	5.24	5.24	5.40	5.40	5.32	22.23
13	5.40	5.40	5.24	5.24	5.32	22.23
14	5.40	5.40	5.24	5.24	5.32	22.23
15	5.40	5.40	5.24	5.24	5.32	22.23
16	5.40	5.40	5.32	5.24	5.34	22.40
17	5.40	5.40	5.16	5.24	5.30	22.06
18	5.32	5.32	5.24	5.24	5.28	21.90
19	5.40	5.40	5.32	5.32	5.36	22.56
20	5.40	5.40	5.32	5.32	5.36	22.56

^a Two samples for each batch.

^b First sample of the batch; two diameter measurements taken to minimize effect of random irregularities.

^c Second sample of the batch; two diameter measurements taken to minimize effect of random irregularities.

TABLE 69. DIAMETER AND AREA OF CONCRETE TEST CYLINDERS:
TWENTY-EIGHT DAY CURE

Batch No. ^a	Diameter (cm)				Average Diameter (cm)	Average Cross- sectional Area (sq cm)
	b	b	c	c		
1	5.29	5.29	5.45	5.45	5.37	22.65
2	5.45	5.45	5.21	5.21	5.33	22.31
3	5.37	5.37	5.45	5.37	5.39	22.82
4	5.37	5.37	5.37	5.37	5.37	22.65
5	5.29	5.29	5.45	5.45	5.37	22.65
6	5.45	5.45	5.29	5.37	5.39	22.82
7	5.29	5.29	5.45	5.45	5.37	22.65
8	5.29	5.29	5.45	5.37	5.35	22.48
9	5.45	5.45	5.29	5.29	5.37	22.65
10	5.45	5.37	5.37	5.37	5.39	22.82
11	5.32	5.32	5.40	5.40	5.36	22.56
12	5.40	5.40	5.24	5.24	5.32	22.23
13	5.32	5.32	5.32	5.32	5.32	22.23
14	5.40	5.40	5.24	5.24	5.32	22.23
15	5.40	5.40	5.24	5.24	5.32	22.23
16	5.40	5.40	5.24	5.16	5.30	22.06
17	5.40	5.40	5.24	5.32	5.34	22.40
18	5.40	5.40	5.16	5.24	5.30	22.06
19	5.40	5.40	5.24	5.24	5.32	22.23
20	5.40	5.40	5.24	5.24	5.32	22.23

^a Two samples for each batch.

^b First sample of the batch; two diameter measurements taken to minimize effect of random irregularities.

^c Second sample of the batch; two diameter measurements taken to minimize effect of random irregularities.

TABLE 70. RESULTS OF COMPRESSIVE CONCRETE STRENGTH TEST
AFTER SEVEN DAYS

Batch No.	Type of Residue ^a	Residue Content (%)	Cross-Sectional Area (sq cm)	Max Load Before Failure (kg)	Time Load Applied (sec)	Strength (kg/sq cm)	Fracture Description
1	Control	0	24.37	3,856	2.0	158.2	Conical, diagonal
2	VSBM	5.2	24.89	4,763	1.8	191.4	Vertical and less diagonal
3		15.8	25.43	3,175	1.6	124.9	Conical, diagonal
4		25.0	25.25	2,948	1.8	116.8	Diagonal
5	NJFA	5.3	25.07	3,402	1.8	135.7	Conical, diagonal
6		15.7	24.72	3,629	1.5	146.8	Vertical, diagonal
7		25.0	24.89	3,856	1.5	154.9	Diagonal
8	VFA	5.2	24.54	2,948	1.6	120.1	Conical with small vertical
9		15.0	24.72	2,495	1.5	100.9	Diagonal
10		24.7	24.37	2,268	1.4	93.1	Diagonal
11	Control	0	22.56	3,855	20	170.88	Conical, diagonal
12	NJSBM	5.3	22.23	2,041	20	91.81	Diagonal, vertical
13		15.2	22.23	2,494	10	112.40	conical
14		25.7	22.23	2,721	10	122.40	Diagonal, vertical
15	EFA	5.2	22.23	3,175	10	142.83	Diagonal, vertical, shearing
16		15.2	22.40	1,814	10	80.98	Diagonal, vertical
17		25.1	22.06	3,401	17	154.17	Diagonal, vertical
18	ESBM	5.3	21.90	1,587	7	72.47	Diagonal, vertical
19		15.2	22.56	1,361	10	60.33	Diagonal, vertical
20		25.1	22.56	1,134	10	50.27	Diagonal, vertical

^a Residue source code presented in Table 6.

TABLE 71. RESULTS OF COMPRESSIVE CONCRETE STRENGTH TEST AFTER TWENTY-EIGHT DAYS.

Batch No.	Type of Residue ^a	Residue Content (%)	Cross-Sectional Area (sq cm)	Max Load (kg)	Time Load Applied (sec)	Strength (kg/sq cm)	Fracture Description
1	Control	0	22.65	3,629	3.0	160.2	Conical and diagonal
2	VSBM	5.2	22.31	4,763	2.5	213.5	Conical and diagonal
3		15.8	22.82	4,536	2.5	198.8	Conical and diagonal
4		25.0	22.65	3,856	2.5	170.2	Conical and diagonal
5	NJFA	5.3	22.65	5,443	3.5	240.3	Conical and diagonal
6		15.7	22.82	5,670	3.0	248.5	Conical and diagonal
7		25.0	22.65	5,897	3.0	260.4	Conical and diagonal
8	VFA	5.2	22.48	4,536	4.0	201.8	Conical and diagonal
9		15.0	22.65	2,948	2.0	130.2	Conical and diagonal
10		24.7	22.82	2,722	3.0	119.3	Conical and diagonal
11	Control	0	22.56	5,443	8.0	241.0	Conical and diagonal
12	NJSBM	5.3	22.23	2,722	10.0	122.4	Conical and diagonal
13		15.2	22.23	3,175	6.0	142.8	Conical and diagonal
14		25.7	22.23	3,856	8.0	173.5	Conical and diagonal
15	EFA	5.2	22.23	3,629	7.0	163.2	Conical and diagonal
16		15.2	22.06	2,495	5.0	113.1	Conical and diagonal
17		25.1	22.40	1,361	3.0	60.8	Conical and diagonal
18	ESBM	5.3	22.06	3,629	6.0	164.5	Conical and diagonal
19		15.2	22.23	1,814	5.0	81.6	Conical and diagonal
20		25.1	22.23	1,134	5.0	51.0	Conical and diagonal

^a Residue source code presented in Table 6.

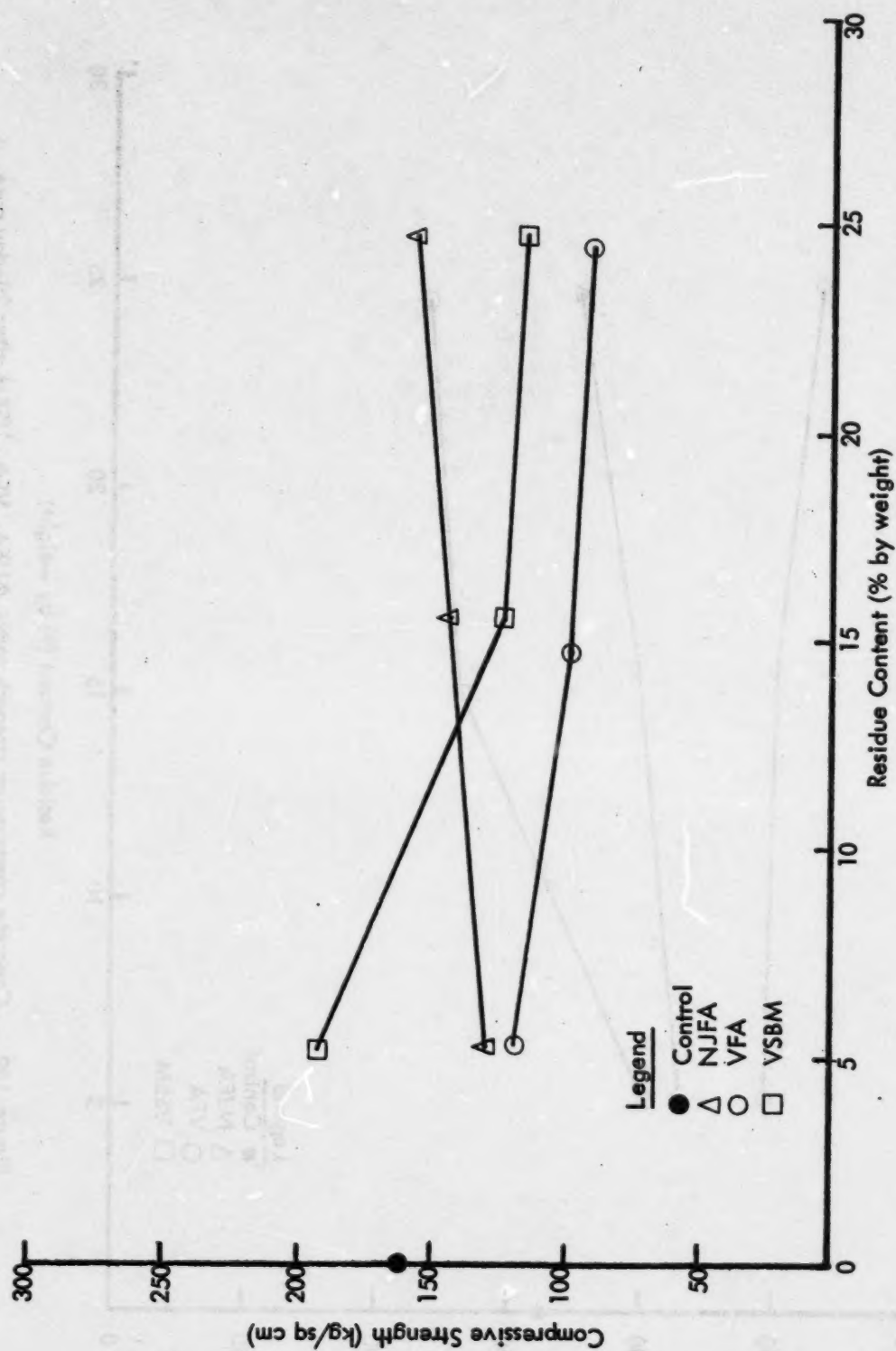


Figure 188. Concrete, compressive strength tests: NJFA, VFA, VSBM after seven day cure.

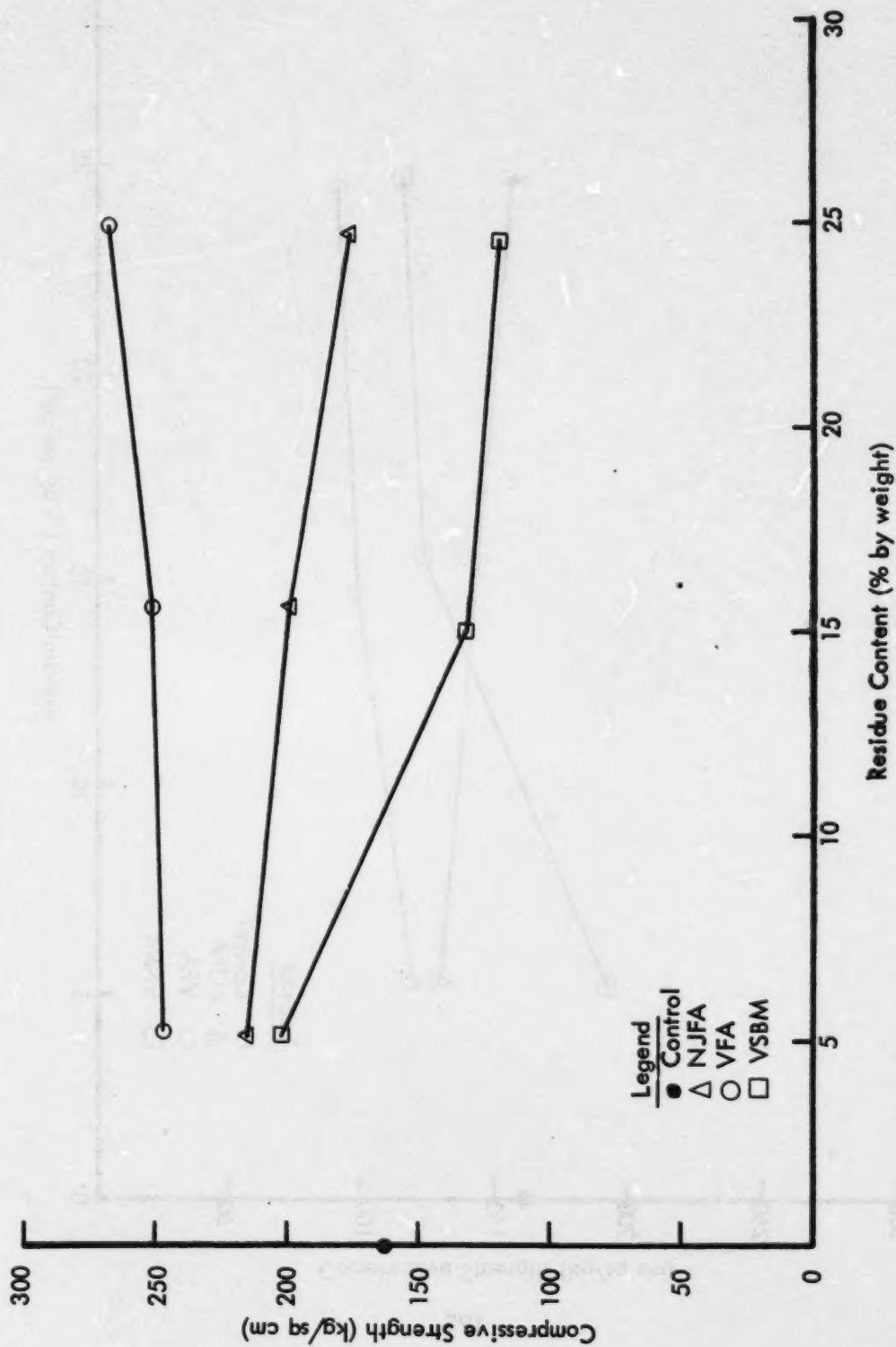


Figure 189 . Concrete compressive strength tests: NJFA, VFA, VSBM after 28-day cure.

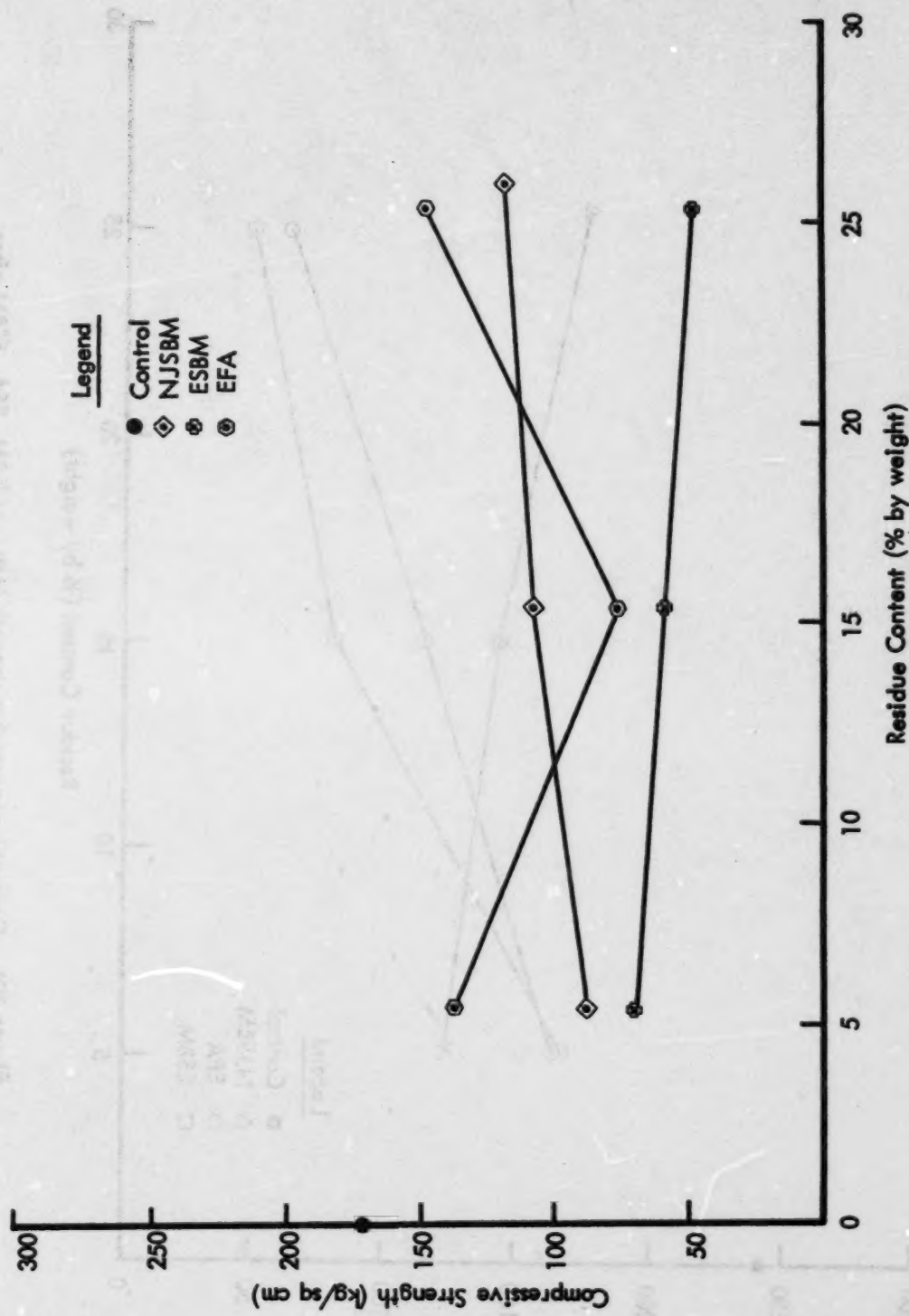


Figure 190. Concrete compressive strength tests: NJSBM, ESBM, EFA after seven day cure.

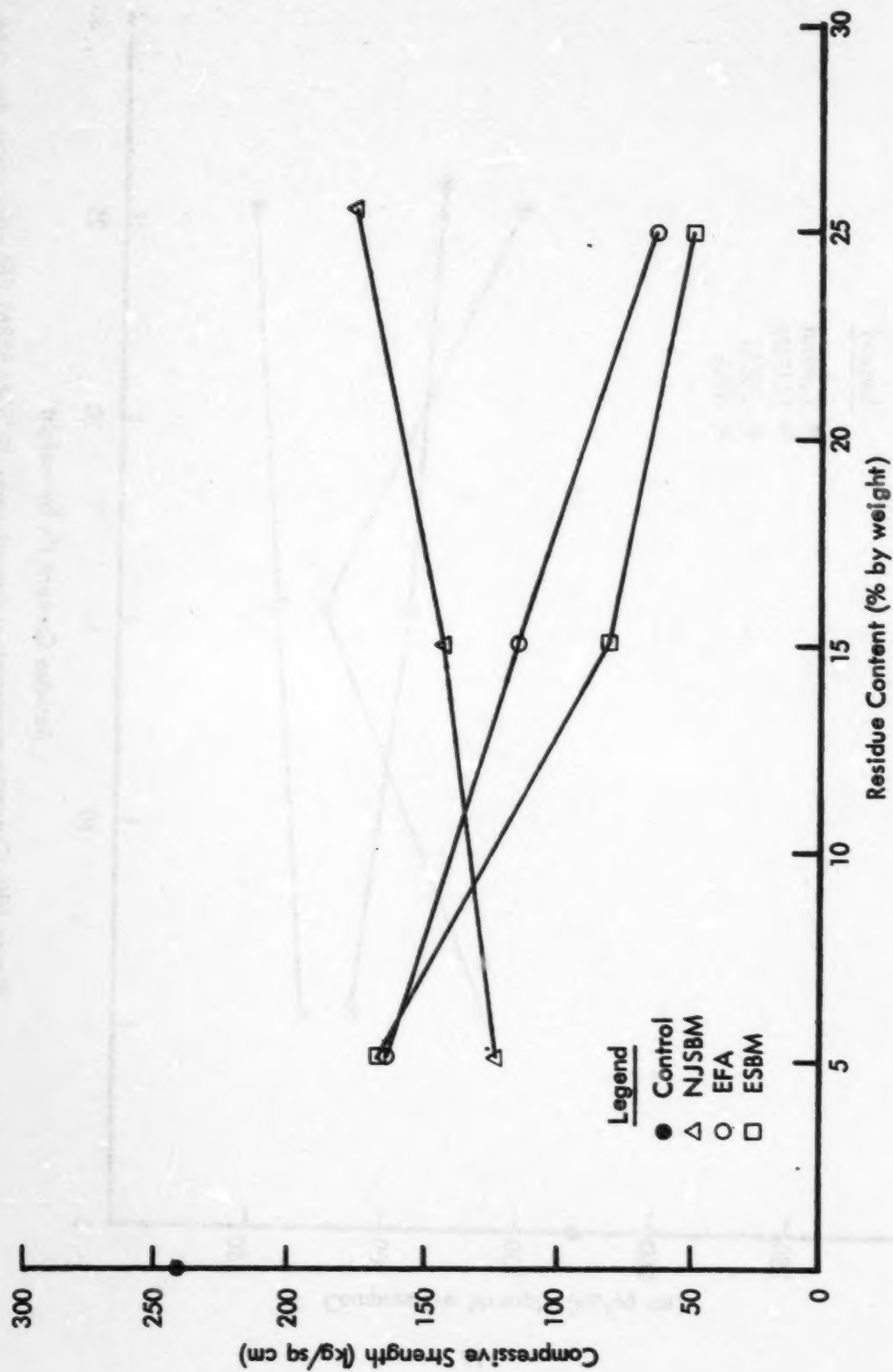


Figure 191 . Concrete compressive strength tests: NJSBM, EFA, ESBM after 28 day cure.

TABLE 72. ASPHALT SAMPLE COMPOSITIONS

Number of Samples	Sample Composition, Percent by Weight			
	Asphalt	Aggregate	Fly Ash or Bed Material	Other Components
12	8	92	--	--
24	8	72	20	--
24	8	47	45	--
24	8	--	92	--
4	8	82	--	10 cement
24	8	--	82	10 cement
4	8	82	--	10 lime
24	8	--	82	10 lime
4	8	92	--	0.24-7*HCL
24	8	--	91.76-85	0.24-7* HCL
<u>68</u>				

* Depending on type of residue



Figure 192 . Result of reaction between residues and emulsified asphalt.

Results. In most cases, substitution of fluidized-bed combustion residues for aggregate did not have a significant beneficial or adverse effect on asphalt compressive strength (see Figures 193 through 196). In several cases, test specimens containing New Jersey spent bed material showed significantly increased strength (e.g., specimens 7 day cure/90 percent residue, 29 hour cure/45 percent residue). In some instances a major reduction in strength occurred (e.g., 7 day cure/82 percent NJFA).

Samples showed large increases in strength when other treatment additives (portland cement, lime or hydrochloric acid) were also included. Replacement of 10 percent by volume of residues with portland cement increased strength from 200 to 300 percent. Replacement with lime similarly increased compressive strength. The strength increase was more than with comparable cement samples when short curing times were used, but less than for comparable cement samples following longer curing times. Neutralization of residue pH with hydrochloric acid also resulted in some increased sample compressive strength.

Potential Agricultural Application of FBC Residues

Plants, to complete their life cycle successfully, require some trace zinc, copper, iron, manganese, boron, chlorine, and aluminum, as well as large quantities of oxygen, carbon, hydrogen, nitrogen, phosphorus, potassium, magnesium, and calcium. The former group of elements is called the micronutrients and the latter, the macronutrients. Any material which contains these nutrients in plant-available form has potential value as a soil conditioner. Fly ash and spent bed material contain most of the micronutrients and some of the macronutrients in plant-available form, as shown in Tables 17 to 20, which present the results of residue chemical characterizations. Residues, because of composition and particle size, may be a good soil conditioner with considerable nutritive value.

Residues could also be used as liming material to reduce soil acidity. Soil acidity develops in humid regions (such as the eastern United States) where the calcium and magnesium may be gradually leached; it is accelerated by crop removal and cultivation. Soil pH is a major determinant of plant growth. Most plants grow best between the range of 7.0 to 7.5, hence both high and low pH's may be detrimental.

In acid soils, large amounts of iron, aluminum, manganese, copper, zinc, and boron may enter into solution and be adsorbed on the surface of the soil particles in a form that plants can readily assimilate. High levels of soluble manganese, iron, aluminum, and boron may be toxic to crops, but liming can correct this condition. In contrast, molybdenum is more soluble in alkaline soils than in acid soils, and thus uptake of this micronutrient may be increased with liming. However, if soil has a pH greater than 8.0, most of the trace elements are fixed in the soil matrix and are unavailable to plants.

The potential for residue agricultural applications was evaluated in a series of small-scale plant growth tests. Table 73 presents the test schedule.

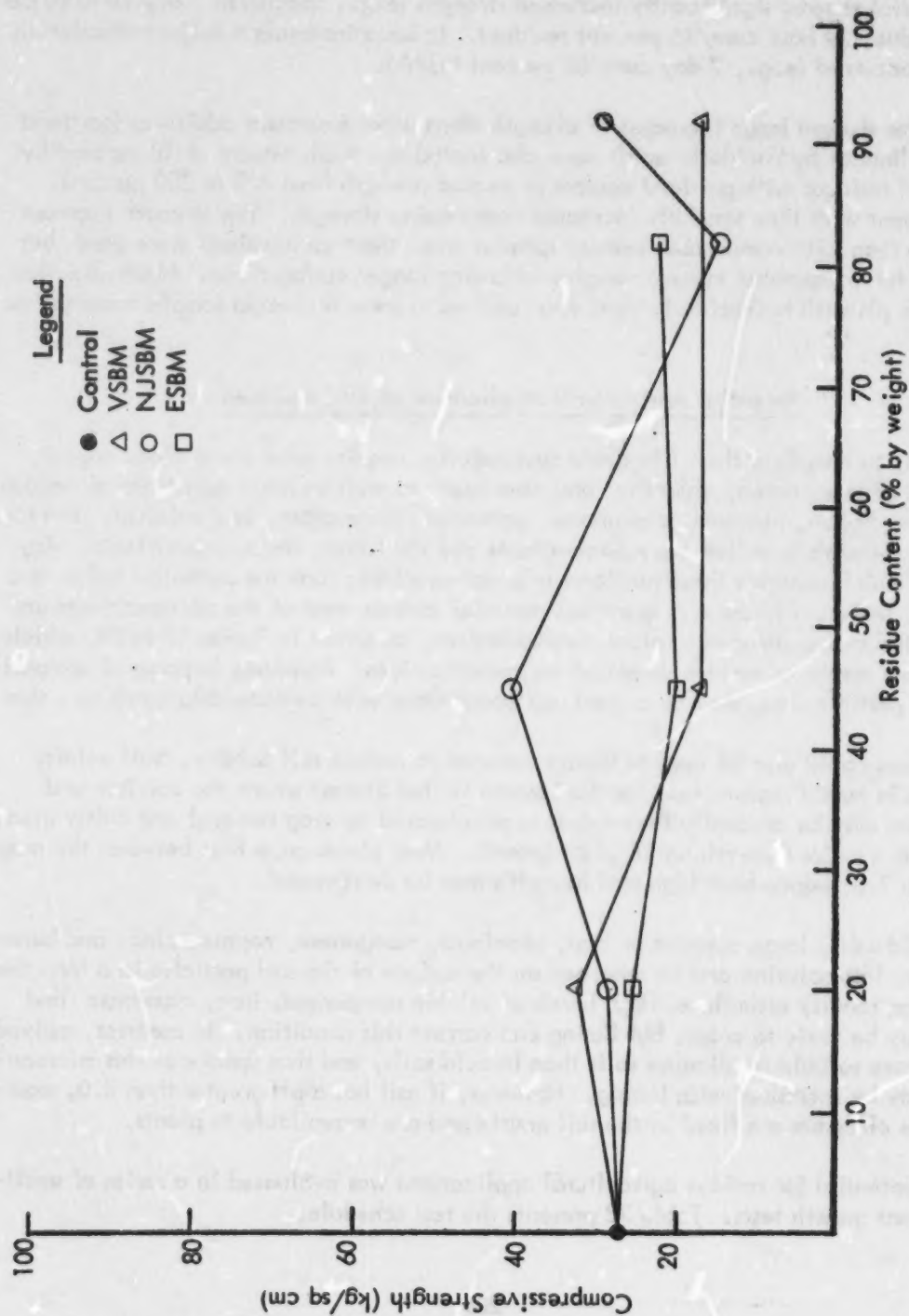


Figure 193. Asphalt compressive strength tests: VSBM, NJSBM, ESBM after 29 hour cure.

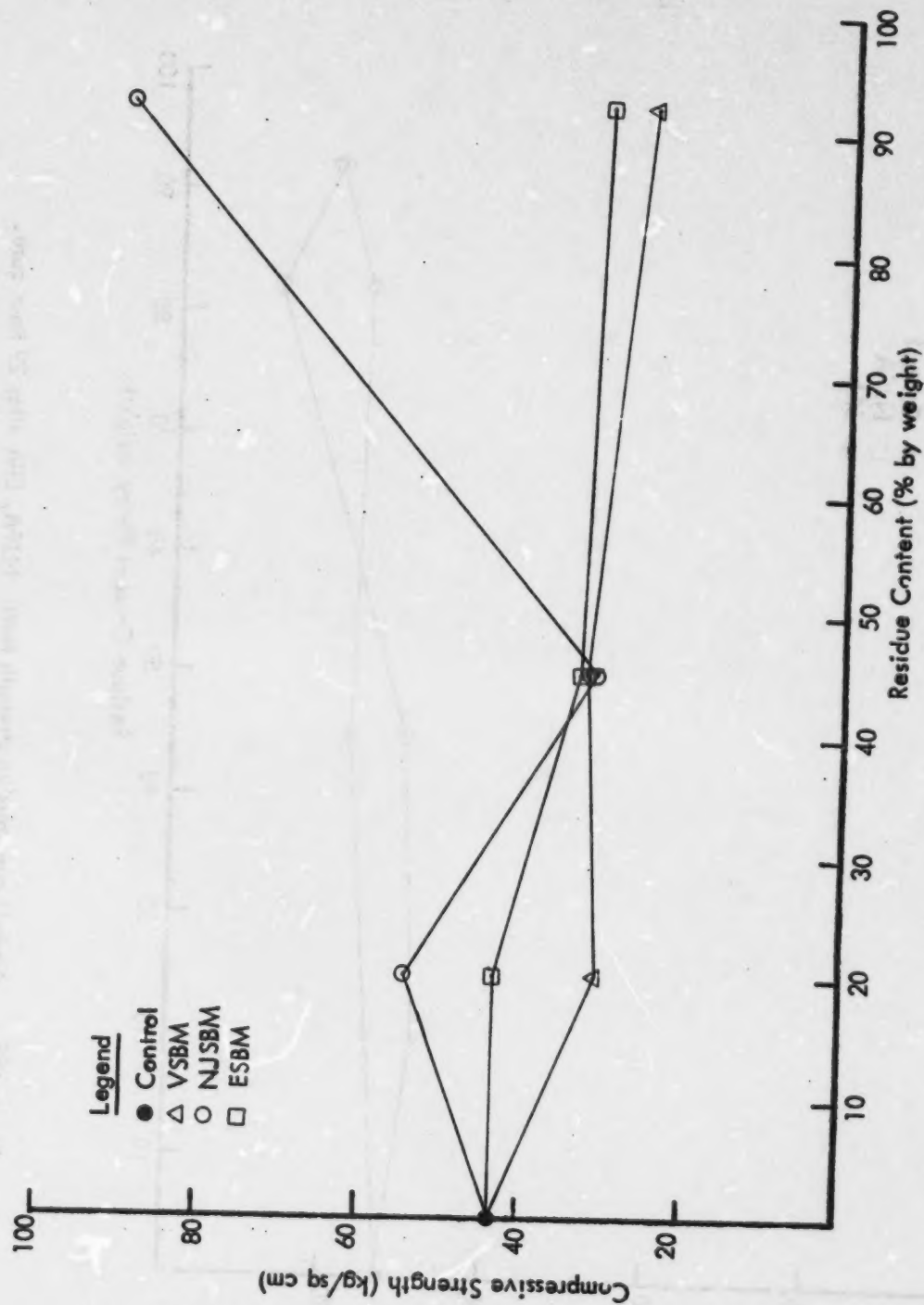


Figure 194. Asphalt compressive strength tests: VSBM, NJSBM, ESBM after seven day cure.

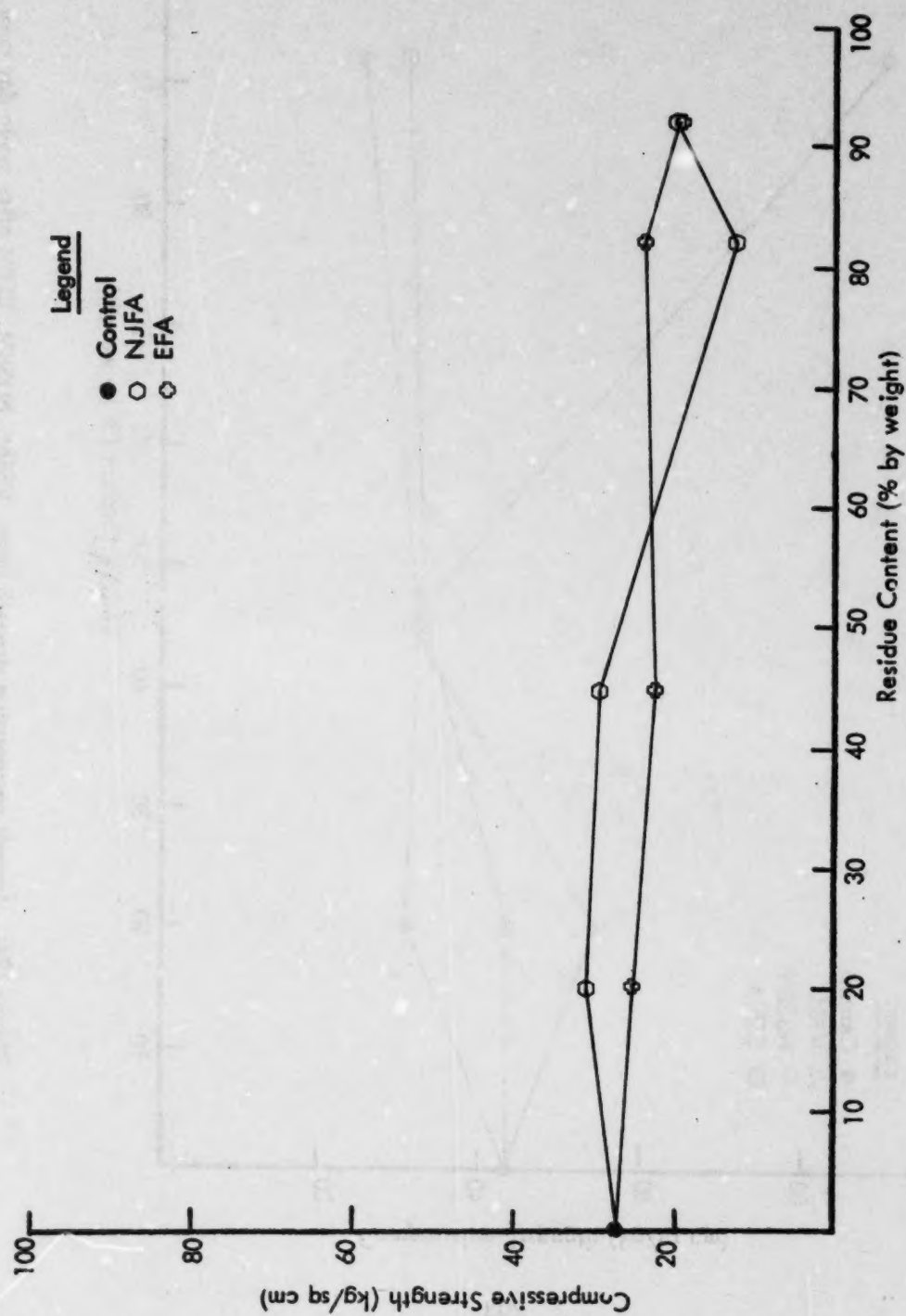


Figure 195. Asphalt compressive strength tests: NJFA, EFA after 29 hour cure.

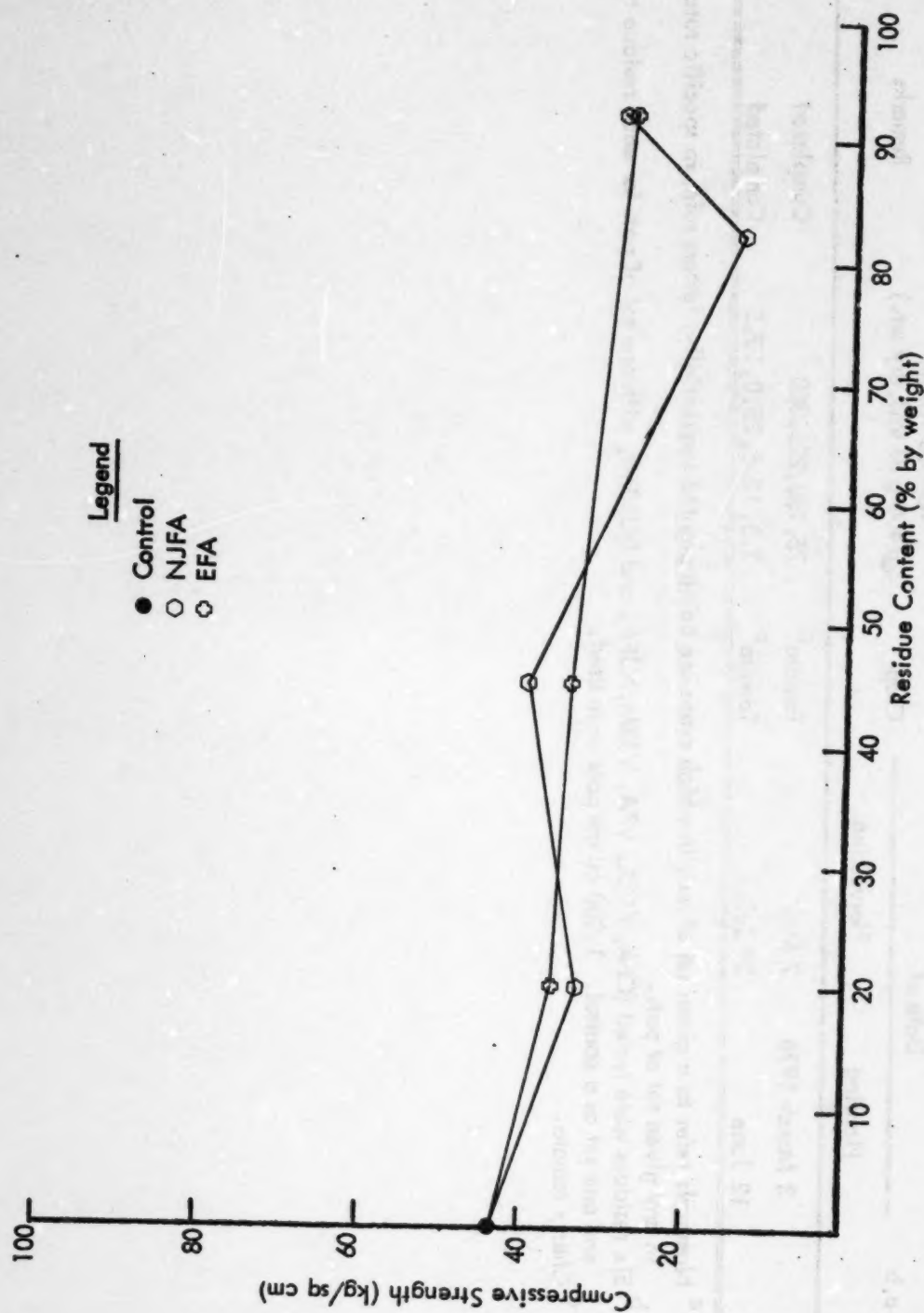


Figure 196. Asphalt compressive strength tests: NJFA, EFA after seven day cure.

TABLE 73. PLANTING SCHEDULE FOR AGRICULTURAL TESTS

No. ^{a,b}	Date of		Crop	Residue Weight (g/400 g of soil, dry wt.)	Remarks
	Planting	Harvesting			
1	3 March 1976	7 May	Tomato ^c	75, 150, 225, 300	Completed
2	12 June	29 July	Tomato ^c	2.5, 12.5, 25.0, 37.5	Completed

^a Numerals refer to a given set of pots in which crops are being planted sequentially; letters refer to specific rotation in any given set of pots.

^b Six residues were tested (CFA, FSFA, VFA, VSBM, NJFA, and NJSBM), with one set of pots for each residue type, and one set as a control. 1,000 cu cm pots were used.

^c Cherry tomato.

Experiment 1.

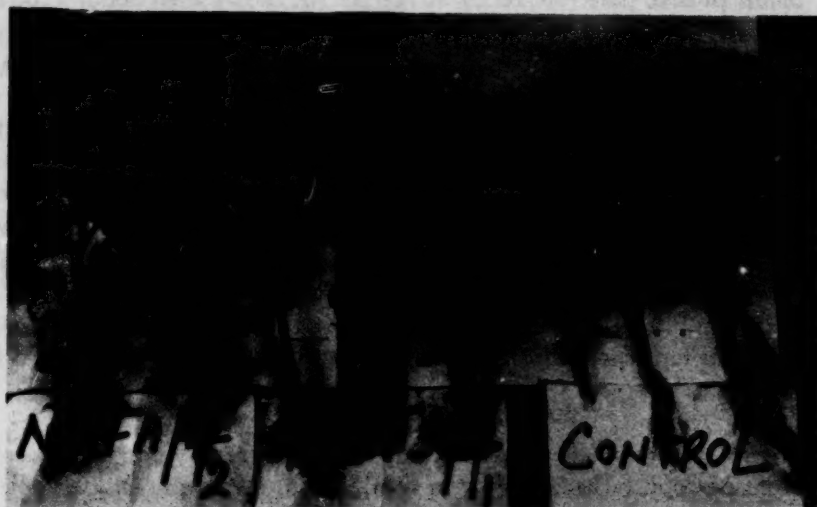
Procedure. Small plastic pots (10.26 by 10.26 by 10.26 cm with about 1.061 cu cm volume) were filled with a commercial potting mixture (Supersoil). The average weight of potting mixture used was about 400 grams. The pots were too small to permit the test plants to complete their entire life cycle. Residues were mixed into the potting mixture at application rates of 75, 150, 225, and 300 grams per pot, which corresponds to field application rates of 67.2, 134.4, 201.7, and 268.9 kkg per hectare. Six residues were tested: CFA, FSFA, VFA, VSBM, NJFA, and NJSBM (these are identified in Chapter 1, Table 6). There were two control pots, and a total of 50 pots used. Fertilizer was surface-applied to each of the soil/residue (and control) mixtures: one gram of ammonium sulfate as a source of nitrogen and one gram of monobasic potassium phosphate as a source of phosphate and potassium. These fertilizers were applied in two equal doses of 0.5 grams each. The first application was made two weeks after planting, and the second four weeks after planting.

Germinated cherry tomato seeds were planted (3 March 1976); each pot was subsequently thinned to one plant per pot. There were two replications for each residue application rate; this was done to reduce the impact of genetic and environmental variability on the test results. The tomato plants were irrigated once a week. The plants were harvested on May 7, 1976.

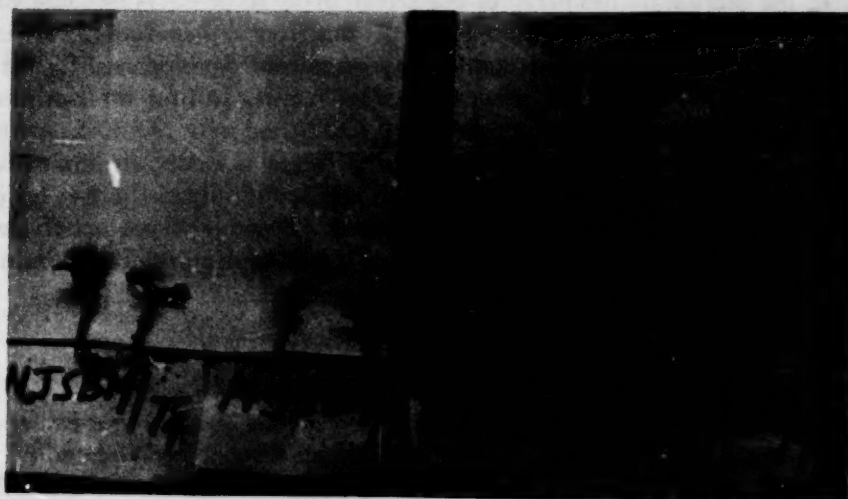
Results. The results are shown in Figure 197 and 198. (T_1 represents the lowest application rate and T_4 the highest). No pictures are shown of CFA or FSFA because the tomato plants did not grow at all in those fluidized-bed oil gasification residues. The very high soil pH produced by the residues significantly suppressed root development for all residues at all application rates. Also, plant growth was significantly less for the test plants than for the controls, and higher application rates were associated with reduced growth. From this experiment it was concluded that (1) there are differences among the six residues in their effects on plant growth, and (2) at these high application rates there is a significant negative impact on plant growth and root development. Based on these conclusions, a second experiment was devised to test the impact of lower application rates (below 35 kkg per hectare).

Experiment 2.

Procedure. This experiment was identical to the previous one, except as noted. Application rates were 2.5, 12.5, 25.0, and 37.5 grams per pot, corresponding to field application rates of 2.2, 11.2, 22.4, and 33.6 kkg per hectare. Three replications were performed for each application rate, and two controls. There were seventy-four pots used in total. Fertilizer was applied as above and the plants were irrigated once per week, with the exception that of the first three weeks when exceptionally warm weather required irrigation twice per week. Planting occurred on 12 June 1976, and harvesting on 29 July 1976. Above-ground plant tissues were digested and analyzed using the procedures outlined in Appendix A.



Exxon, New Jersey fly ash



Exxon, New Jersey spent bed material

Figure 197. Experiment 1, tomato plant growth.



PER, Virginia fly ash



PER, Virginia, and Exxon, New Jersey fly ash

Figure 198. Experiment 1, tomato plant growth.

Results. Photographs taken of the plants just before harvesting are shown in Figure 199. The impact of residue application on plant growth is given quantitatively in Table 74 and graphically in Figures 200 and 201. Table 74 presents the wet and dry weight and the ratio of wet to dry weight.

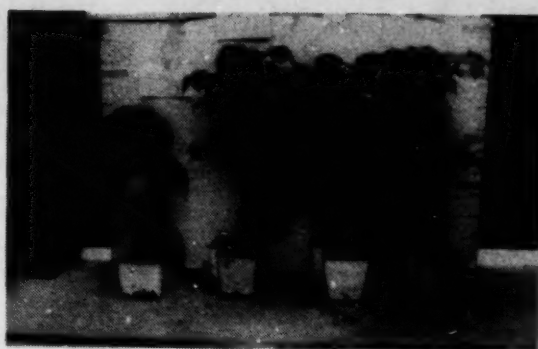
The results show a significant improved growth response at application rates of 2.2 and 11.2 kkg per hectare for CFA, FSFA, VFA, and NJFA residues. For these same residue types, growth was repressed at 22.4 and 33.6 kkg per hectare application rates. There was a significant positive growth response at all application rates for the VSBM, and NJSBM residues. Percent dry weight increased from 5 to 80 percent for all residue types for application rates of 2.2 and 11.2 kkg per hectare. For CFA, percent dry weight decreased significantly at a 22.4 kkg per hectare application rate.

The potting mixture used in the experiments had a high level of humic acid and, consequently, a low pH (about 5.5). Since the fly ash and spent bed residues are quite alkaline, adding them to the potting mixture raised soil pH (as shown in Tables 75 and 76). The effect on plant growth plotted against soil pH is presented in Figure 202. The figure shows growth improvements (in comparison to the control) when pH was in a range from 6.2-7.8. This improvement is almost certainly at least partially the result of the residues having increased the pH to more optimal values.

The biodegradation of the residue materials by soil microorganisms may also have released micronutrients for plant uptake. If the pH adjustment mechanism were beneficial, one would expect it would make little difference what type and source of fluidized-bed residue were used. But, as Figure 202 shows, there is considerable variability in results for a given pH. Since the various residues differ substantially in chemical composition, it may be tentatively assumed that this dispersion reflects differences in the availability and quantity of nutrients that were provided to the plants in the residues.

Results for chemical analyses of plant tissues are given in Table 77, and graphically in Figures 203 to 208. Tomato plants grown on residue-treated soil showed significantly lower concentrations of analyzed heavy metals than the control plants. This effect is undoubtedly pH-related. For the most part, sulfate concentrations were not significantly different for treated and control plants. Exceptions were FSFA/T₂, VFA/T₄, NJFA/T₂, and NJSBM/T₁, T₃, and T₄. There was no significant difference in the concentration of magnesium between the control and residue-treated vegetation except for NJFA/T₂. All residue-treated vegetation (except VFA/T₂) showed significantly higher concentrations of calcium, which is associated with improved cell turgidity. Although the calcium concentration was higher in the treated plants, they did not show signs of a toxic calcium level.

From this experiment, it appears that residues applied at reasonably low concentrations increased the soil pH and therefore restricted the uptake of heavy metals by plants, and even reduced their concentration in plant tissues. Excessive concentrations of heavy metals in plants utilized for direct or indirect human consumption are undesirable; specifically any food with an increased cadmium metal content is considered dangerous for human



Control T₁ T₃ T₄
PER, Virginia fly ash



Control T₁ T₂ T₃ T₄
PER, Virginia spent bed material



Control T₁ T₂ T₃ T₄
Exxon, New Jersey fly ash



Control T₁ T₂ T₃ T₄
Exxon, New Jersey spent bed material



Control T₁ T₂ T₃ T₄
Esso, England cyclone fly ash



Control T₁ T₂ T₃ T₄
Esso, England fines, stack fly ash

Figure 199. Experiment 2-A, tomato plant growth.

TABLE 74. EXPERIMENT 2-A: TOMATO PLANT
GROWTH RESULTS

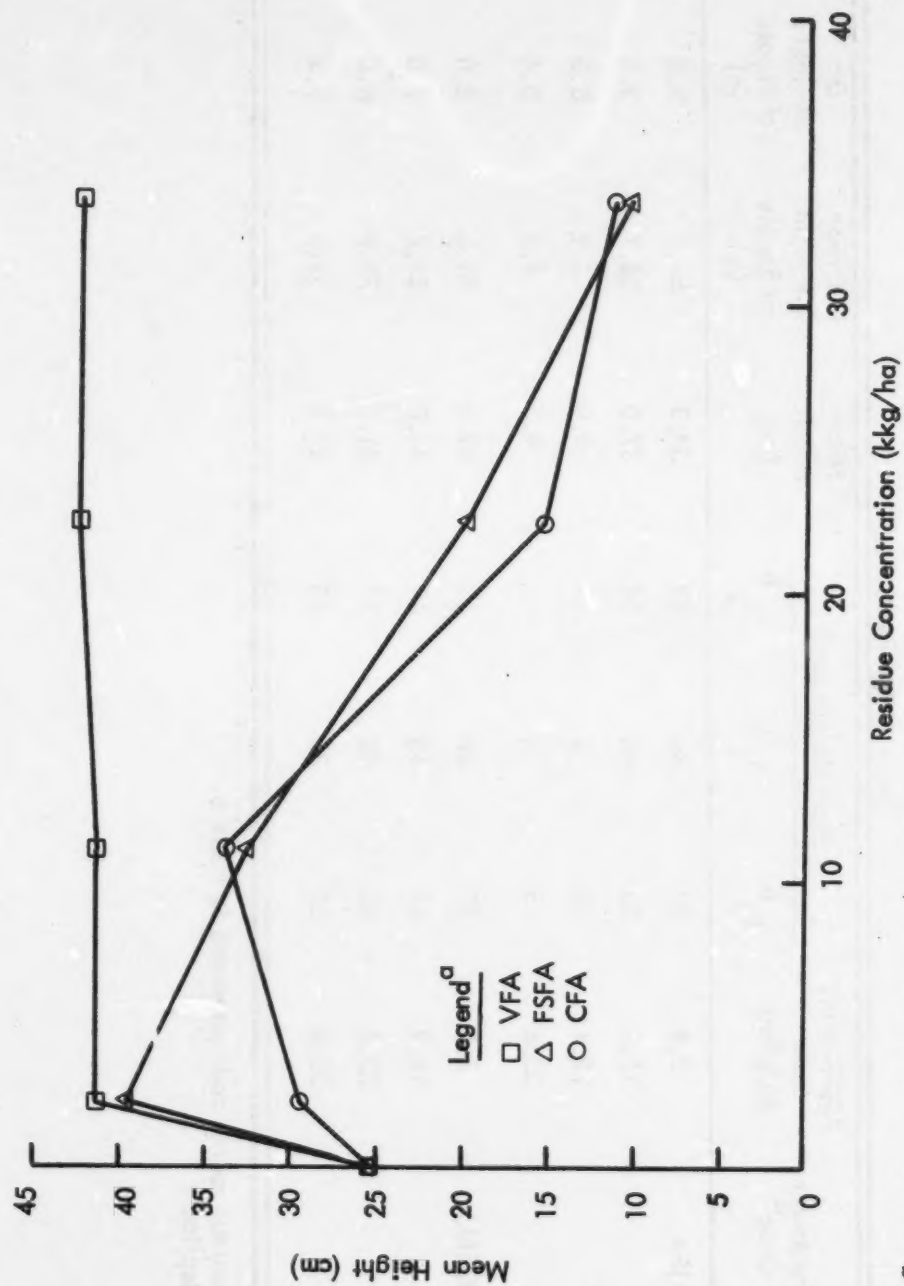
Treatment Code ^a	Application Rate (kg/ha)	Plant Height (cm)			Mean Height (cm)	Green Weight of Shoots (g)	Dry Weight of Shoots (g)	Ratio of Dry to Wet Weight (%)
		R ₁ ^b	R ₂ ^b	R ₃ ^b				
Control	0	31	28	17	25.3	40.0	3.5	8.75
CFA	2.2	30	30	29	29.6	31.1	4.9	16.55
	11.2	34	33	35	34.0	57.5	5.2	15.29
	22.4	15	20	11	15.3	11.4	0.7	4.57
	33.6	5	16	13	11.3	5.3	0.5	9.43
FSFA	2.2	33	35	41	39.6	62.0	5.5	13.88
	11.2	27	35	36	32.6	55.0	4.7	14.41
	22.4	19	22	19	20.0	15.0	1.4	7.01
	33.6	14	9	8	10.3	13.0	0.9	8.73
VFA	2.2	36	43	45	41.3	48.8	5.6	13.55
	11.2	37	43	45	41.3			
	22.4	36	43	47	42.6	60.2	6.3	10.46
	33.6	43	37	43	42.3	64.3	4.2	6.53
VSBM	2.2	43	45	40	42.6	64.4	6.4	9.93
	11.2	39	40	41	40.6	61.6	5.7	9.25
	22.4	35	35	36	35.3	28.3	1.9	6.71
	33.6	35	43	37	38.7	40.0	3.7	9.25

(continued)

TABLE 74 (Cont.)

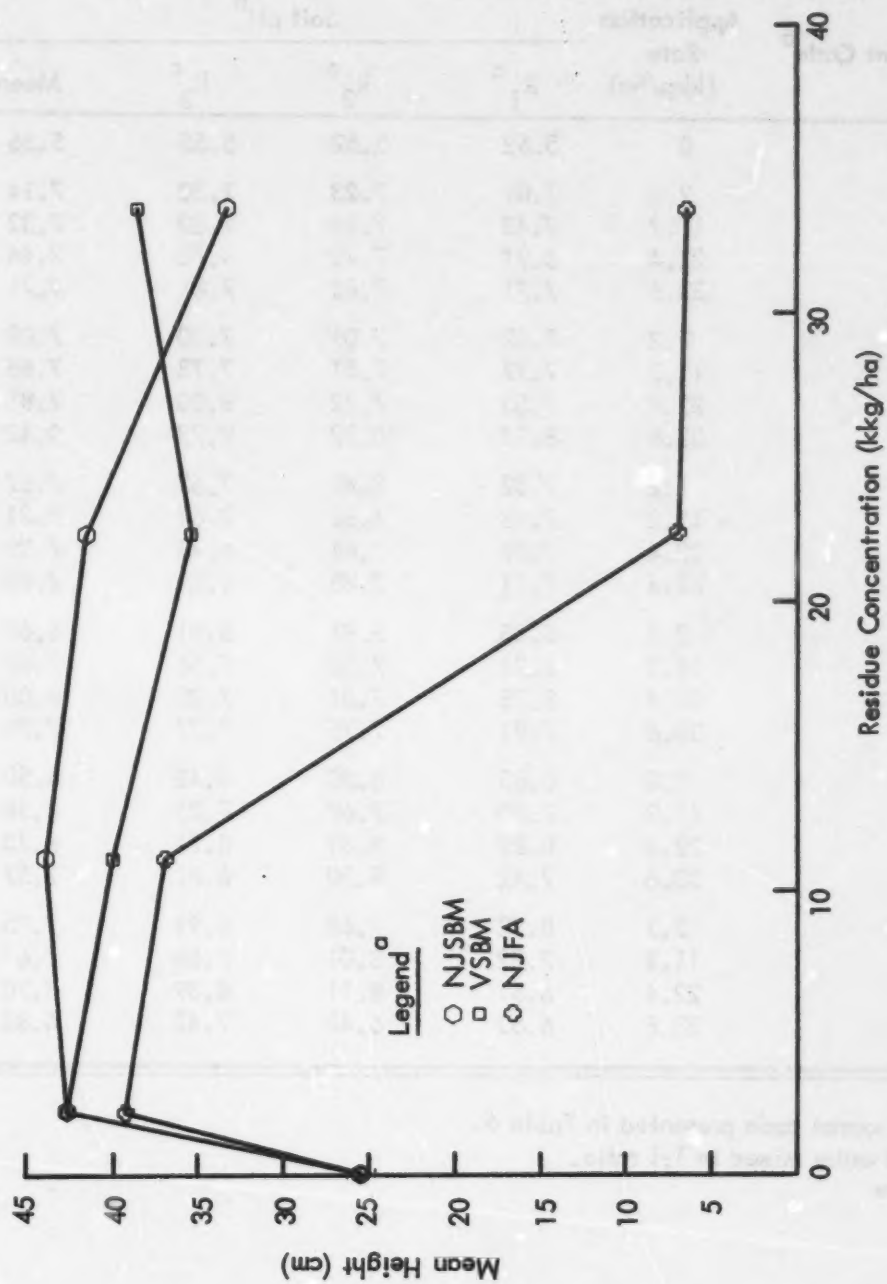
Treatment Code ^a	Application Rate (kg/ha)	Plant Height (cm)			Mean Height (cm)	Green Weight of Shoots (g)	Dry Weight of Shoots (g)	Ratio of Dry to Wet Weight (%)
		R ₁ ^b	R ₂ ^b	R ₃ ^b				
NJFA	2.2	43	36	39	39.3	55.1	5.4	9.80
	11.2	33	40	34	37.0	38.7	3.4	8.78
	22.4	10	8	3	7.0	3.9	0.3	7.69
	33.6	5	8		6.5	4.8	0.4	8.33
NJSBM	2.2	37	39	42	39.3	35.6	3.0	7.63
	11.2	45	43	44	44.0	35.2	3.0	8.52
	22.4	43	45	37	41.6	75.9	6.0	7.90
	33.6	37	32	30	33.3	33.6	3.2	9.52

^a Residue source code presented in Table 6.^b Replicate



^a See Table 6 for explanation of letter code.

Figure. 200. Mean tomato plant height, Experiment 2: VFA, FSFA, CFA.



^a See Table 6 for explanation of letter code.

Figure 201. Mean tomato plant height: Experiment 2: NJSBM, VSBM, NJFA.

TABLE 75. pH OF SOIL-RESIDUE MIXTURE

Treatment Code ^a	Application Rate (kkg/ha)	Soil pH ^b			
		R ₁ ^c	R ₂ ^c	R ₃ ^c	Mean
Control	0	5.52	5.62	5.55	5.56
CFA	2.2	7.01	7.23	7.20	7.14
	11.2	7.43	7.22	7.32	7.32
	22.4	6.91	7.72	7.70	7.44
	33.6	7.71	7.62	7.81	7.71
FSFA	2.2	7.07	7.01	7.20	7.09
	11.2	7.72	7.51	7.73	7.65
	22.4	7.53	7.72	8.20	7.81
	33.6	8.22	10.32	9.73	9.42
VFA	2.2	7.52	8.49	7.62	7.87
	11.2	7.18	6.82	7.64	7.21
	22.4	7.59	7.81	6.48	7.29
	33.6	7.11	7.83	6.31	7.08
VSBM	2.2	6.33	6.91	6.81	6.68
	11.2	8.21	7.26	7.56	7.67
	22.4	8.73	7.51	7.92	8.05
	33.6	7.91	7.75	7.72	7.79
NJFA	2.2	6.83	6.50	6.42	6.58
	11.2	7.80	7.69	7.25	7.58
	22.4	8.29	8.51	8.21	8.33
	33.6	7.42	8.50	6.81	7.57
NJSBM	2.2	8.72	7.62	6.91	7.75
	11.2	7.32	8.01	7.68	7.67
	22.4	6.61	8.11	8.39	7.70
	33.6	6.63	6.42	7.42	6.82

^a Residue source code presented in Table 6.^b Soil and water mixed in 1:1 ratio.^c Replicate

TABLE 76. pH OF SOIL RESIDUE MIXTURE AFTER CROP 2 HARVEST

Treatment Code ^a	Application Rate (kg/ha)	Soil pH ^b			
		R ₁ ^c	R ₂ ^c	R ₃ ^c	Mean
Control		6.7	7.1	6.9	6.90
CFA	2.2	6.73	6.70	7.30	6.91
	11.2	7.54	6.90	7.10	7.18
	22.4	7.17	7.60	7.40	7.39
	33.6	7.13	7.80	8.20	7.90
FSFA	2.2	7.21	7.20	6.80	7.07
	11.2	7.80	7.60	7.40	7.60
	22.4	8.04	8.00	7.00	7.68
	33.6	8.33	7.50	8.50	8.11
VFA	2.2	7.14	7.60	7.40	7.38
	11.2	6.34	7.10	6.90	6.78
	22.4	7.15	6.80	7.20	7.05
	33.6	6.76	6.30	6.20	6.42
VSBM	2.2	5.90	6.60	6.40	6.30
	11.2	7.36	6.64	7.33	7.11
	22.4	7.82	6.71	7.43	7.32
	33.6	7.31	7.33	7.42	7.35
NJFA	2.2	7.27	6.70	7.30	7.09
	11.2	7.75	7.0	7.0	7.25
	22.4	8.30	8.0	7.70	8.00
	33.6	6.20	6.50	6.50	6.40
NJSBM	2.2	6.24	6.12	6.21	6.19
	11.2	6.81	7.13	6.82	6.92
	22.4	7.66	7.10	6.90	7.22
	33.6	7.35	7.60	7.50	7.45

^a Residue source code presented in Table 6.

^b Soil and water mixed in 1:1 ratio.

^c Replicate

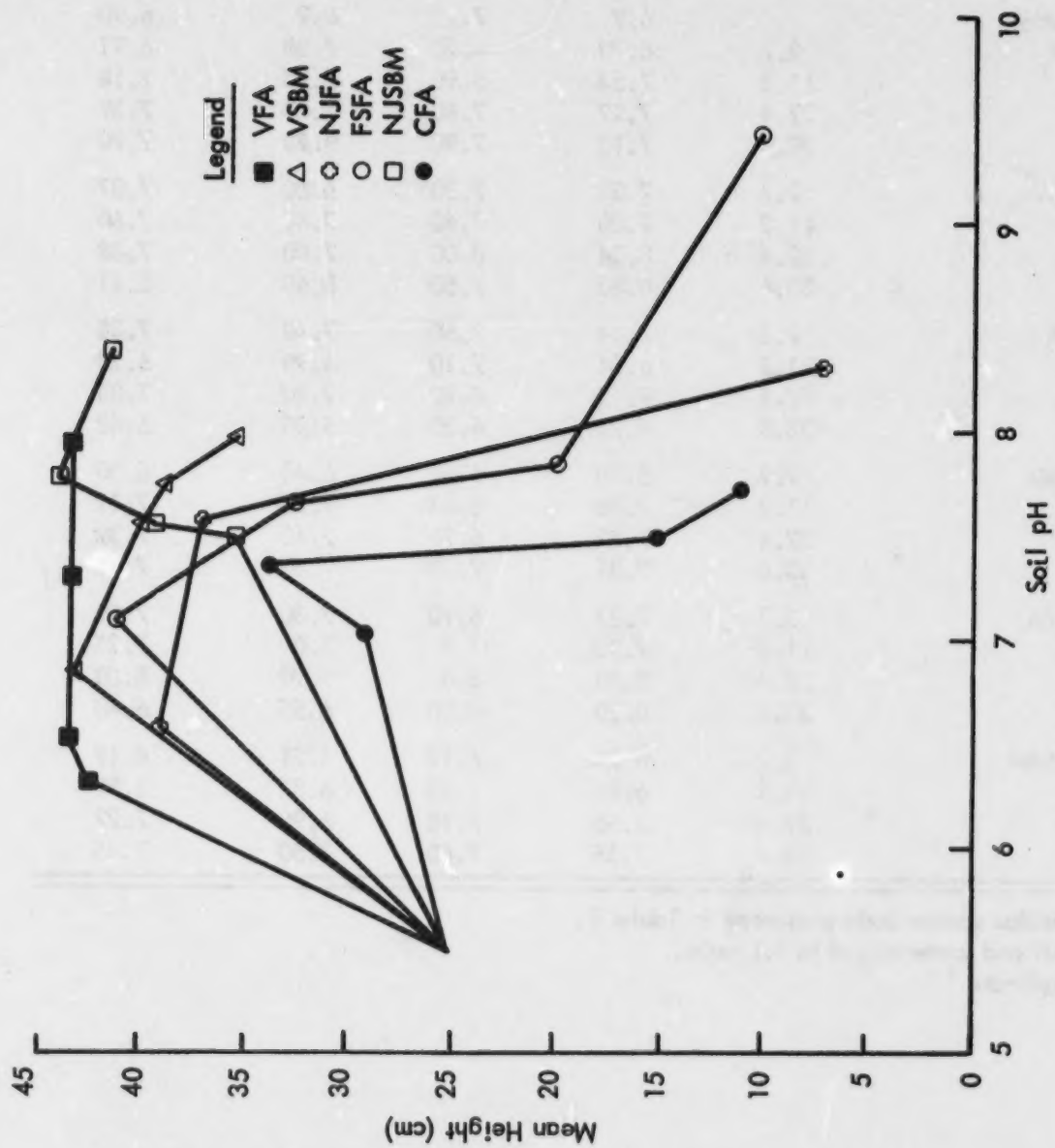


Figure 202.. Tomato plant growth vs. soil pH, Experiment 2.

TABLE 77. TOMATO PLANT DIGESTION ANALYSIS RESULTS FROM EXPERIMENT 2

Treatment	Ca %	Mg %	SO ₄ %	Mn ppm	Zn ppm	Fe ppm
Control	0.08	0.158	1.65	68	51	130
CFA/T ₁	0.19	0.197	1.50	93	20	90
CFA/T ₂	0.19	0.145	1.00	14	2	N.D. ^a
FSFA/T ₁	0.22	0.155	0.60	3	20	N.D.
FSFA/T ₂	1.22	0.202	4.30	14	2	N.D.
VFA/T ₁	0.12	0.153	1.40	18	10	90
VFA/T ₃	0.05	0.151	0.80	17	5	30
VFA/T ₄	0.37	0.148	2.30	6	4	30
VSBM/T ₁	0.17	0.211	1.60	N.D.	2	N.D.
VSBM/T ₂	0.16	0.102	0.50	N.D.	7	40
VSBM/T ₄	0.56	0.140	1.90	N.D.	3	60
NJFA/T ₁	0.12	0.135	0.90	22	6	70
NJFA/T ₂	0.15	0.523	3.75	N.D.	0.1	N.D.
NJSBM/T ₁	0.38	0.182	2.60	16	1	20
NJSBM/T ₂	0.30	0.130	1.60	10	1	20
NJSBM/T ₃	0.86	0.178	3.70	12	N.D.	N.D.
NJSBM/T ₄	0.66	0.170	3.40	N.D.	4	40

^a N.D. = None detected.

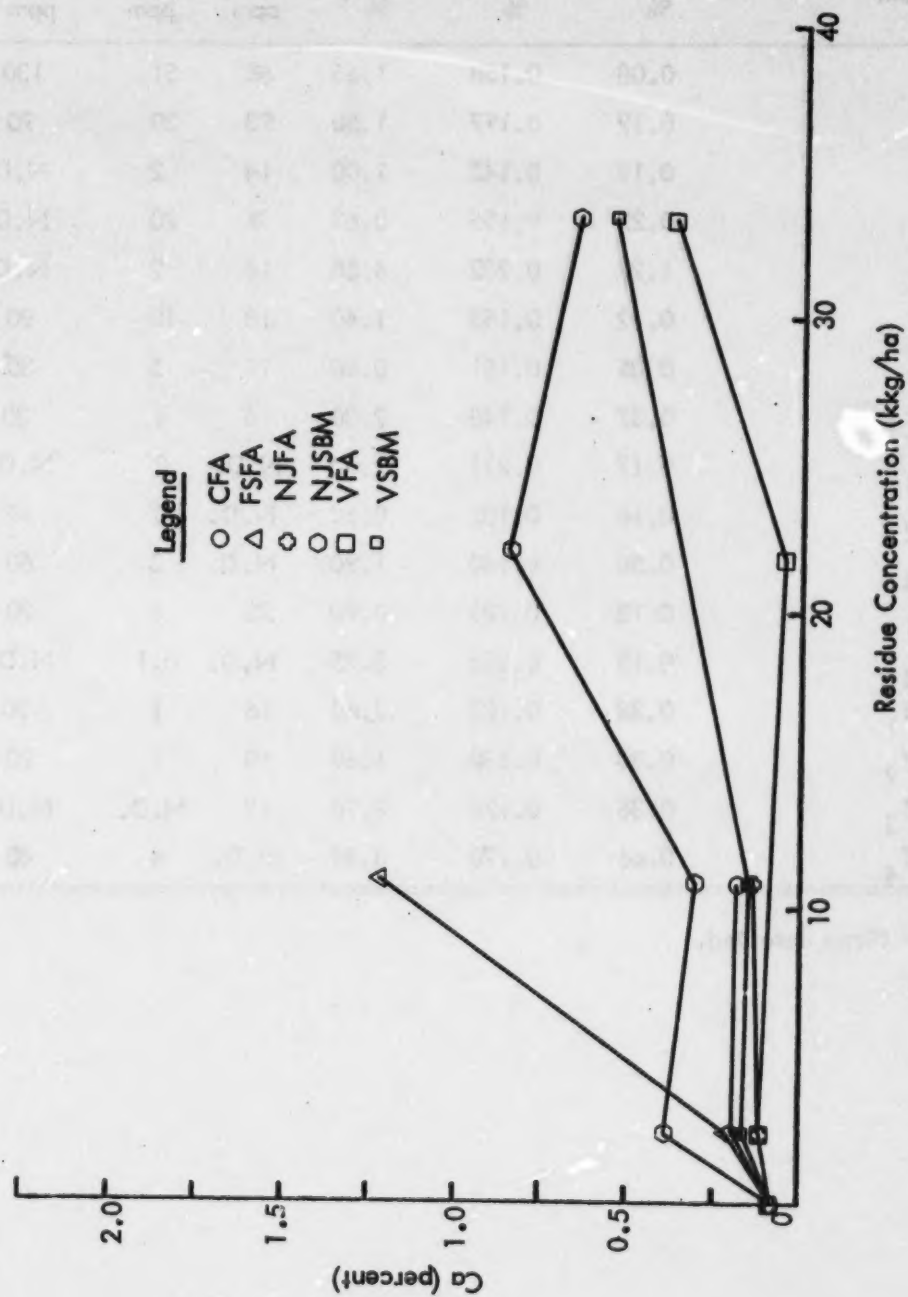


Figure 203. Calcium content in digested tomato plant tissue: Experiment 2.

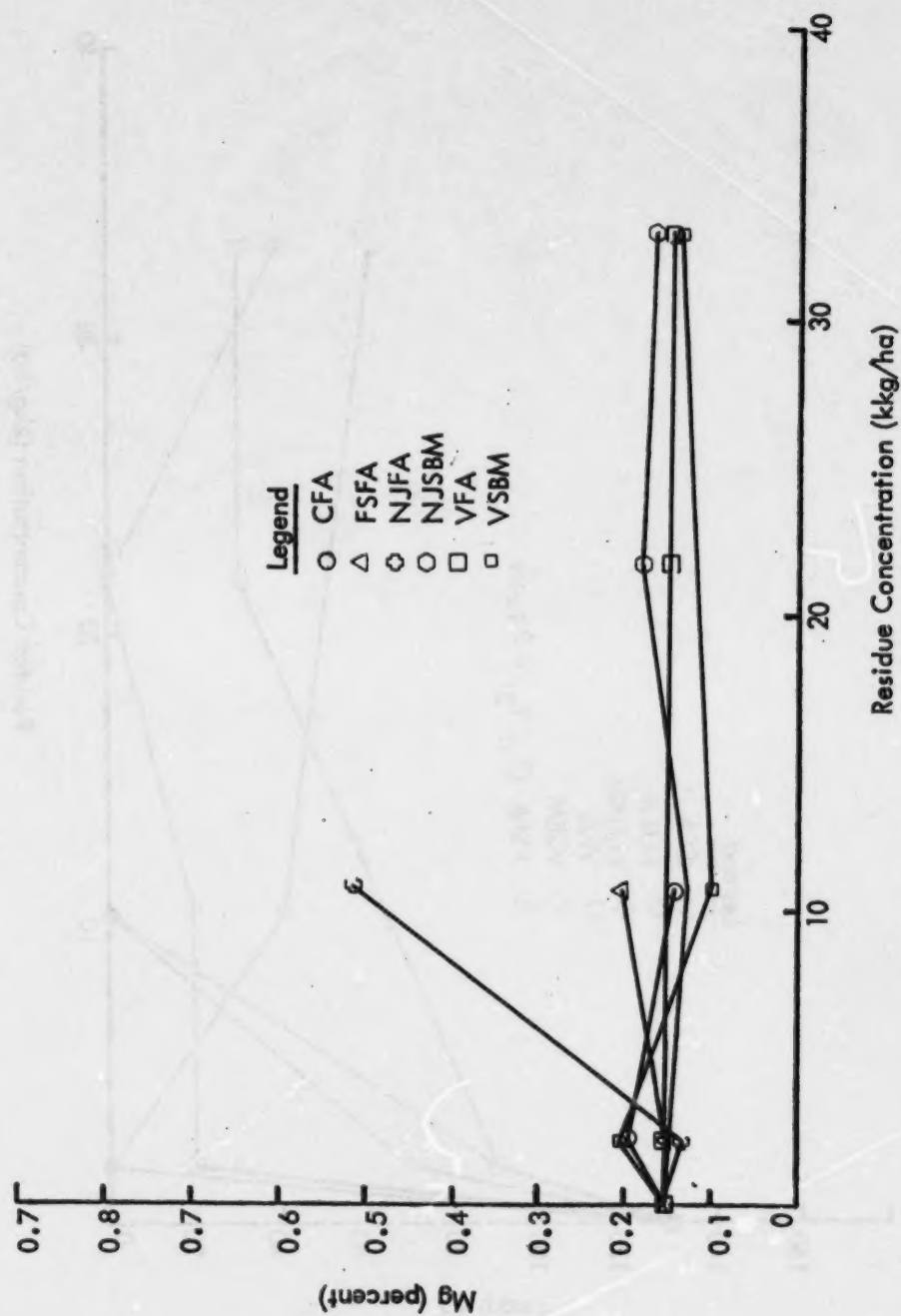


Figure 204 Magnesium content in digested tomato plant tissue : Experiment 2.

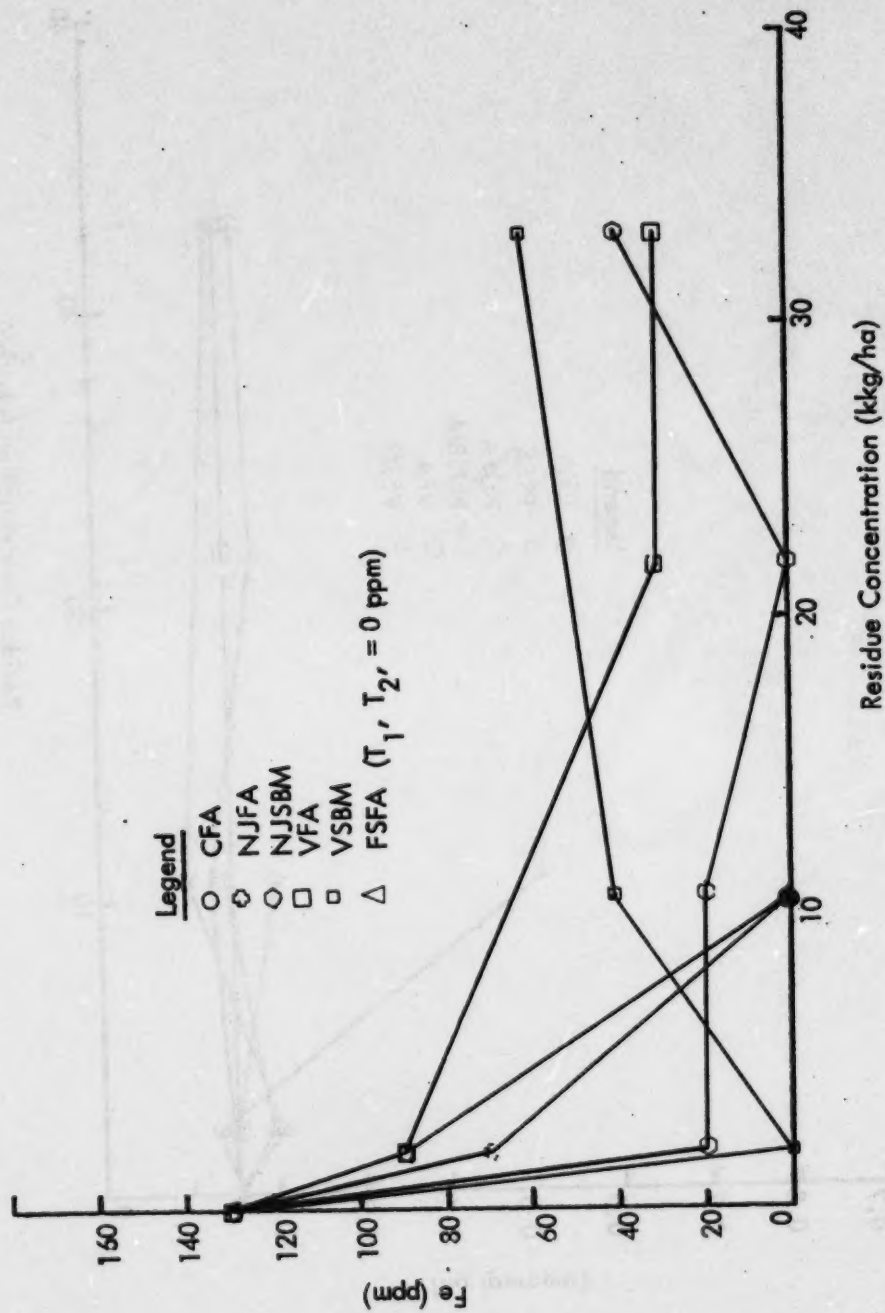


Figure 205 . Iron content in digested tomato plant tissue: Experiment 2.

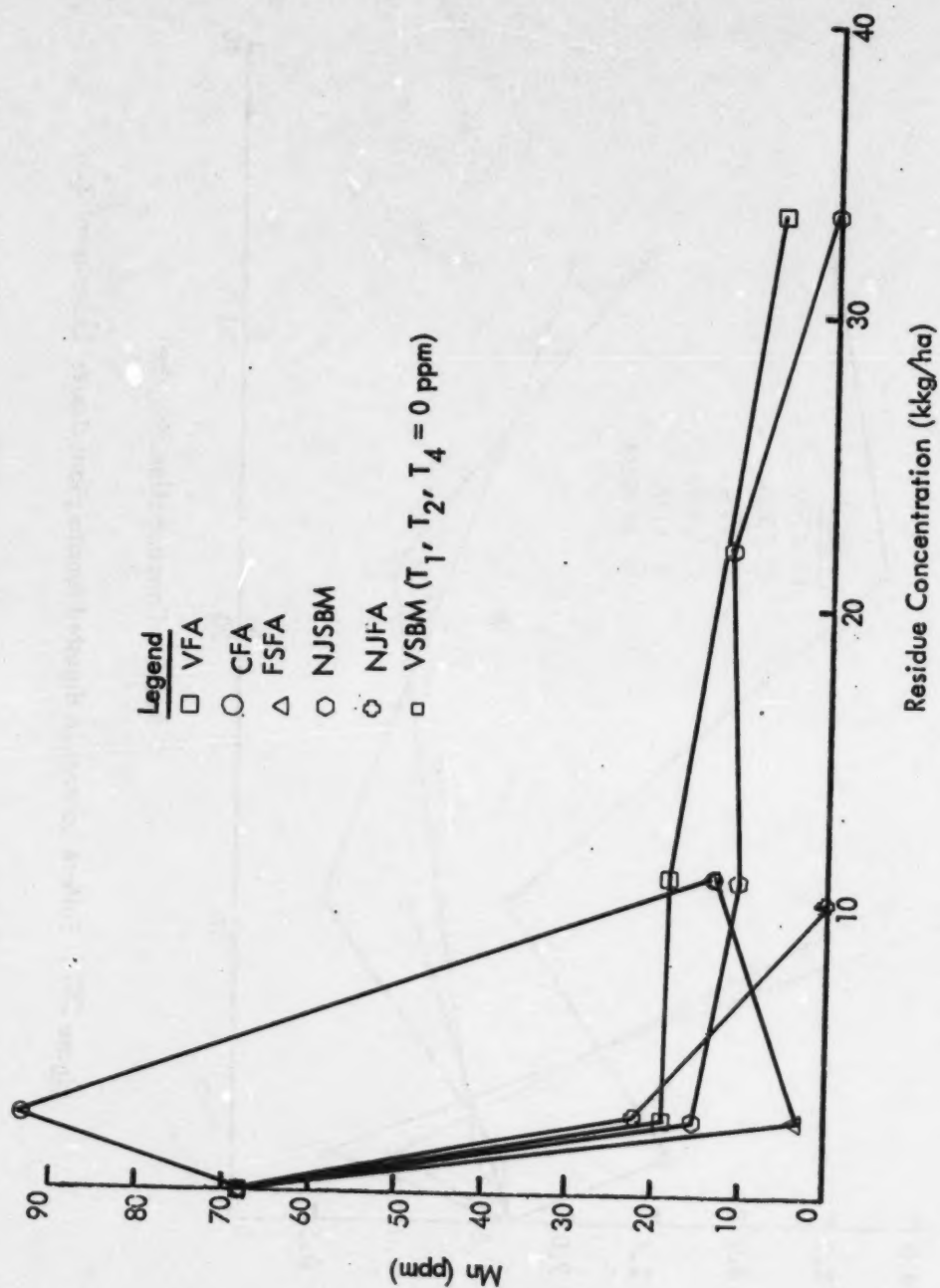


Figure 206 . Manganese content in digested tomato plant tissue: Experiment 2.

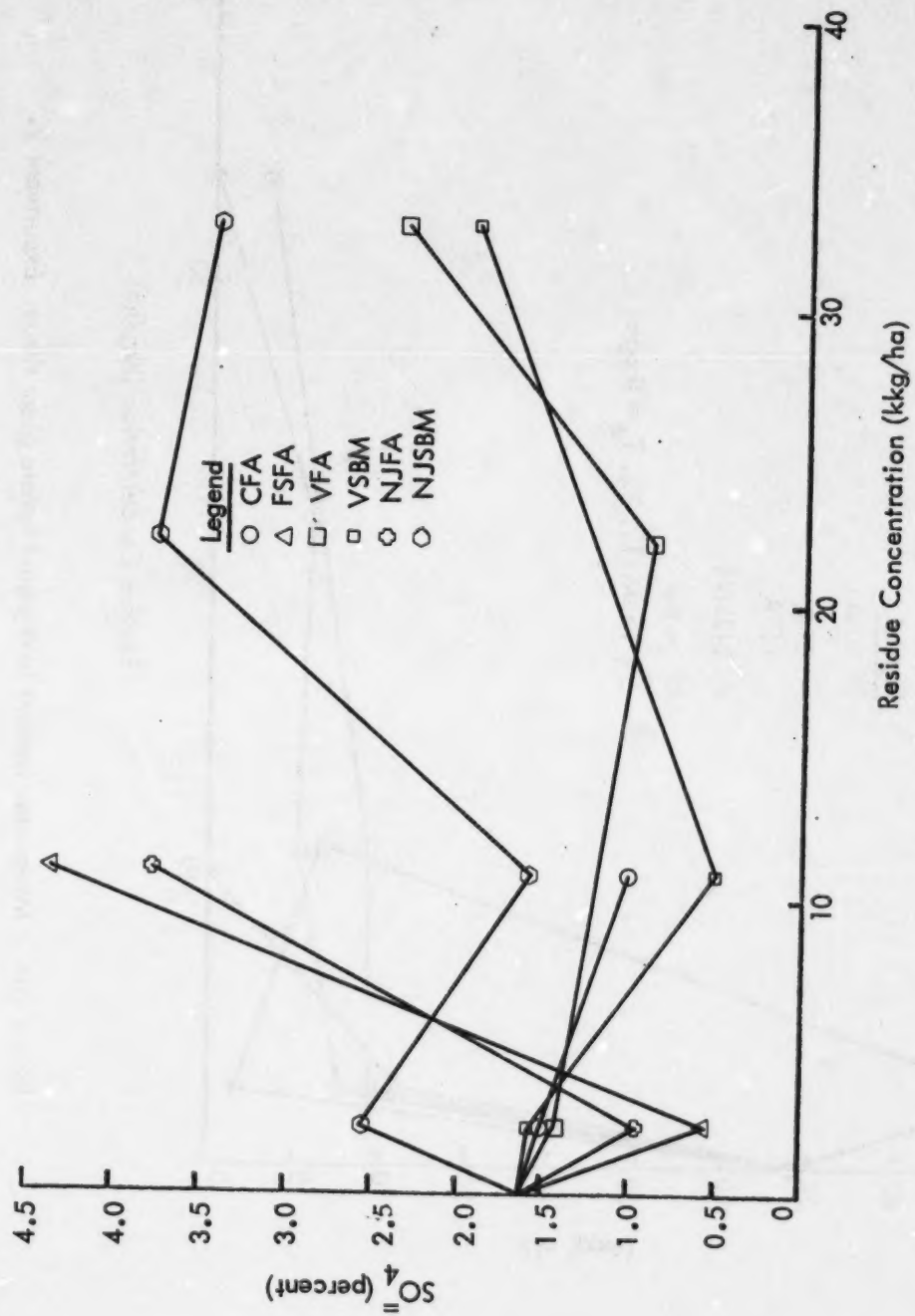


Figure 207. Sulfate content in digested tomato plant tissue: Experiment 2.

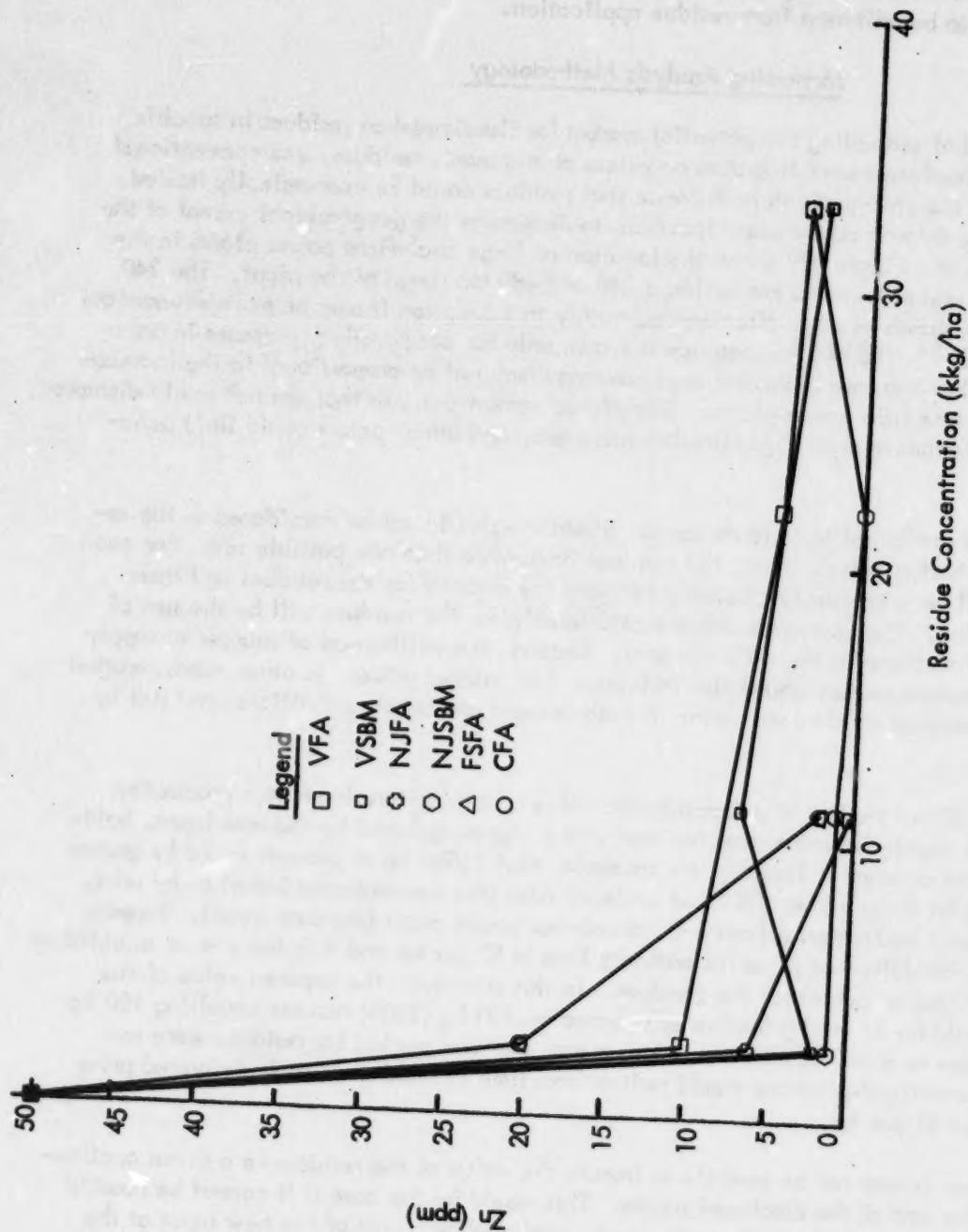


Figure 208 . Zinc content in digested tomato plant tissue: Experiment 2.

consumption. Soils containing low pH, high heavy metal levels, or deficiencies in trace metals appear to benefit most from residue application.

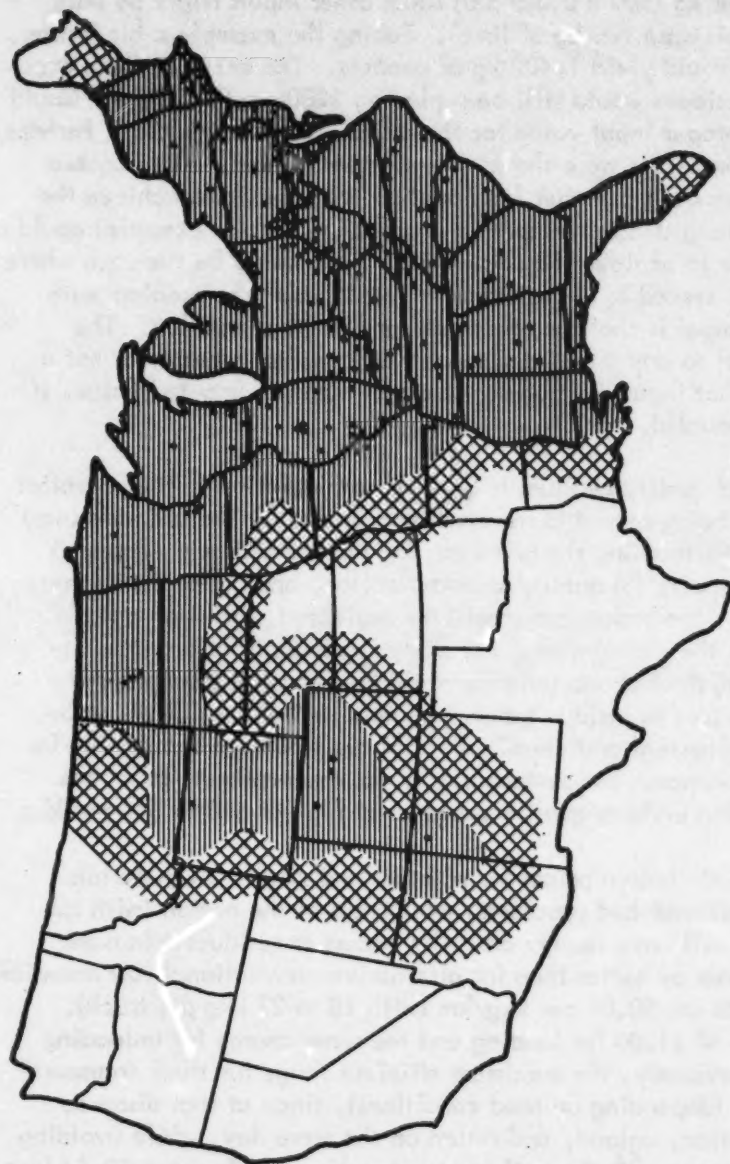
Marketing Analysis Methodology

The method of estimating the potential market for fluidized-bed residues in specific applications involved converting data on prices of transport, residues, and conventional materials into the cost-equivalent distance that residues could be economically hauled, and then using data on power plant locations to determine the geographical extent of the potential market. Figure 209 shows the location of large coal-fired power plants in the United States and adjacent areas within a 240 and 480 km range of the plant. The 240 km distance is shown because after approximately that location it may be more economical to ship by rail.⁵⁴ The 480 km distance is shown only for comparative purposes in order to illustrate that increase in market area coverage may not be proportional to the increase in travel distance from power plants. Established market patterns that are not easily disrupted, price ratio changes as market penetration increases, and other factors could limit penetration.

The value attributed to residues for any given use should not be considered as the estimate of its market price. First, the residues have more than one possible use. For each use there will be a certain relationship between the demand for the residues and their delivered price. The aggregate demand relationship for the residues will be the sum of the demand functions for the different uses. Second, the willingness of sources to supply residues at various prices would also influence their market price. In other words, market price is determined by the interaction of both demand and supply conditions, not just by use value.

The most direct method of estimating the value of a substitute input to a production process is to impute its value from the cost of the inputs replaced by the new input, holding the output constant. Suppose, for example, that 1,000 kg of peanuts could be grown on a given plot using either 100 kg of ordinary lime (the conventional input) or by using 200 kg of spent bed material from a fluidized-bed power plant (the new input). Suppose further that the delivered price for ordinary lime is \$2 per kg and that there is no established market (and thus no price) for the residues. In this situation, the imputed value of the residues would be \$1 per kg (delivered), based on 200 kg (\$200) residue equalling 100 kg (\$200) of lime as a soil conditioner. This means that if a market for residues were established, a rational producer would switch from lime to residues if their delivered price was less than \$1 per kg.

Sometimes it may not be possible to impute the value of the residues in a given application from the cost of the displaced inputs. This would be the case if it cannot be readily determined how much of which inputs can be replaced by a unit of the new input at the given output level. In such a case, it may be possible to impute the value of the residues from their impact on output. Several examples are given below to illustrate the method and its pitfalls.



Legend

- Power plant site
- ▨ 0-240 km from power plant
- ▩ 241-480 km from power plant

Source: 54.

Figure 209 . Distance to large U. S. coal-fired power plants.

If the experimental data available indicated that 200 kg of residues yielded 1,000 kg of peanuts and that the price of peanuts is \$0.50 per kg, we could not conclude that the value of the residues is \$2.50 per kg ($1,000 \times 0.50/200$). It is likely that, even without any residues, some peanuts would have been produced. Suppose, then, that without any inputs 500 kg of peanuts would have been produced. Again, this does not imply that the value of the residues is \$1.25 per kg ($500 \times 0.50/200$) since other inputs might be able to achieve the same result (in this case 100 kg of lime). Taking the example a bit further, suppose that 300 kg of residues would yield 1,400 kg of peanuts. The value of the extra output would be \$200 and the residues would still be replacing \$200 worth of lime. Could we conclude from this that the proper input value for the residues is \$1.33 per kg? Perhaps, but only if several restrictive conditions were shown (or assumed) to hold. The imputed value would be wrong, for instance, if a higher lime application rate could achieve the same yield. It would also be wrong if a third input (a source of sulfur, for example) could be used in conjunction with lime to achieve the same yield. This would be the case where the residues serve a function not served by the input being replaced. The problem with imputations based on output changes is that they may misrepresent the situation. The appropriate question with respect to any imputed value for an input is, whether or not a rational producer would adopt that input if its price were less than the imputed value. If not, then the imputed value is invalid.

The delivered cost of standard quality residues is a prime consideration to the potential user. Most of the ash currently being reused is removed by a broker (or the ultimate user) at no cost to the utility. In that situation, the price (or cost) to the user will represent charges for (1) pick-up, (2) transport, (3) quality standardization, and (4) profit to the broker. For purposes of analysis, the broker profit will be neglected, although a fixed percentage could be included in the calculation. For many reuse applications it is important that the chemical and physical characteristics of the residues are standardized within reasonable limits. Variations in residue parameters may limit its usability. Obviously, for some applications, physical and chemical variations would be significant; for others they may make little difference. For certain uses it has been estimated that the delivered price of fly ash assuming uniform quality could be as high as \$10 to \$14 per kkg.

Shipping costs will affect the delivered prices for residues and virgin raw materials. With widespread adoption of fluidized-bed processes, most areas of the nation (with the possible exception of the West) will have ready, close-by access to residues. In many cases, access to residues may even be better than for alternative conventional raw materials. Approximate truck transport costs are \$0.04 per kkg/km (with 18 to 27 kkg per truck). For short hauls, an extra charge of \$1.00 for loading and the same charge for unloading has been assumed. As stated previously, the maximum efficient range for truck transport is estimated to be about 240 km (depending on road conditions), since at that distance the driver can get to his destination, unload, and return on the same day, while avoiding overtime and other costs for a layover.⁵⁴ For rail transport, a car-lot is about 50-54 kkg and transport cost about \$0.02 per kkg/km, plus an additional fee for shaking the car to complete unloading. It should be noted that rail freight rates discriminate about 20 percent against secondary materials (such as fly ash) in comparison to primary materials.

Although current practice provides zero-cost pickup of residues from some power plants, it may be reasonable to assume that utilities must generally pay to have them removed. The value of the fly ash to them is not zero, but rather is less than zero by the unit they have to pay to dispose of the residues. The cost of land disposal has been, and is projected to continue increasing in response to: (1) the impact of general inflation on transport and handling costs, (2) increasing scarcity of acceptable, close-by landfill sites, and (3) increasing strict environmental regulations on waste disposal. Disposal cost will vary from place to place, but can generally range from \$3-6 per kkg. Costs may be even higher if special treatment is necessary prior to disposal. For example, chemical fixation followed by landfilling is one method of treatment for the residues from limestone flue-gas desulfurization systems. The experience of several firms with that process is shown in Table 78.

Thus, certain applications not judged economically feasible if the residue cost was zero at the power plant site may be acceptable if the power plant paid for removal of the residues. Because of the difficulties in estimating (1) what the utility would be willing to pay for residue removal, and (2) the cost of insuring adequate residue quality, in the remainder of the analysis, it will be assumed that these two factors balance one another and that the residues are available at a zero cost.

Economic Analysis of Specific Applications

Concrete.

Substantial research (discussed above) exists showing that adding fly ash to concrete can improve the characteristics of the concrete. The fly ash can be used to replace aggregate and, because it is also a pozzolan, a portion of the portland cement. Based on preliminary research results, concrete mixtures with approximately 5 percent residue content display improved strength characteristics. Table 79 compares the composition of the optimal concrete mix (as determined in the testing program) containing residues to that of a standard concrete mix (used as a control for the tests). The table also estimates the cost savings from using residues as a partial substitute for aggregate and portland cement which would result if residues were available at a free delivered price. This saving would be \$0.50 per kkg of concrete. Since 53 kg of residues would be used in one kkg of concrete, the imputed value of the residues would be \$0.50/53 kg or about \$0.01 per kg of residue. This implies that a concrete producer would (all other things equal) use the residues if their delivered price were about \$0.01 per kg or less. To the extent that the improved characteristics imparted by the residues to the concrete results in a higher market price for the concrete, the producer may be willing to pay in excess of \$0.01 per kg delivered for the residues. Assuming an imputed value of \$0.01 per kg, a rail freight rate of \$0.02 per kkg-km, and a zero f.o.b. price for the residues at the power plant site, residues could be rail-hauled a distance up to 472 km and remain competitive. By truck they could be economically transported about one-half that distance.

Asphalt.

Coal ash has been used successfully as a replacement for aggregate in asphalt for some

TABLE 78 . SLUDGE FIXATION COSTING ESTIMATES
All values are condition and site dependent

Source	Cost (\$/kkg, 50% solids)		Remarks
Commonwealth Edison Company, Will County Station	6.50		On-site disposal--vendor quote
	9.41		Current estimate ^a
	5.78		Best experience ^a
	11.00		Worst experience ^a
	5.50		Target ^a
Duquesne Light Company, Phillips Station	7.98		Total disposal
International Utilities Conversion Systems, Inc.	1.65-2.75		On-site disposal
Chemfix	5.50		On-site disposal
Dravo Corporation	1.65-3.30		Total cost to customer; includes pump- ing to 10 mi

^aCompany Operation - on-site disposal; excludes capital costs.

TABLE 79. RESIDUE VALUE FOR USE IN CONCRETE

Item	Composition (%)		Value (\$/kkg) ^a		Cost Reduction (\$/kkg)
	Control	Residue Added	Control	Residue Added	
Concrete compo- nent					
Fly ash	0	5.3	0	b	0
Aggregate	71.5	64.7	3.55	3.21	0.34
Portland cement	15.2	14.9	8.02	7.86	0.16
Water	13.3	15.1	0	0	0
Total	100	100	11.57	11.07	0.50

^a Based on a delivered cost (in Los Angeles) for portland cement of \$52.78/kkg and for aggregate of \$4.96/kkg.

^b Value of residue to be imputed from savings from its use ($\$11.57 - \$11.07 = \$0.50/\text{kkg}$).

time. For example, the West Virginia Department of Highways has found that an asphalt surface coating with a thickness of 5 to 7.5 cm made from dry bottom-ash and emulsified asphalt works satisfactorily and its cost is about half that of conventional asphalt. The low cost results from two factors. First, there is a large, readily available supply of coal ash located conveniently throughout the state. Second, the technology required is simple and the same as needed with conventional asphalt. Ash is loaded into a portable continuous pugmill, frequently located at the power plant site, and mixed with a metered amount of emulsified asphalt. Then it is either loaded directly on trucks or stockpiled for future use. The well-graded ash usually requires no additional blending. Using emulsified asphalt makes heating and drying unnecessary, thus eliminating the need for relatively costly hot bins or dryers.

Other examples of successful use of coal-ash residues in asphalt could be cited. But even though the technology appears simple and sound, use in this application has remained quite limited (approximately 180,000 kkg of residues in 1972).¹³¹ There does appear to be a substantial potential market, however. In comparison to a delivered (Los Angeles) price of aggregate of \$4.96 per kkg, conventional coal-combustion residues could be transported approximately 250 km by rail (at \$0.02/kkg-km) or 125 km by truck (at \$0.04/kkg-km) and be competitive.

Little work has been done on limestone or dolomite modified residues. Wet-collected residues from flue gas desulfurization systems appear to have some promise in asphalt applications. However, if substantial dewatering or drying is required prior to use, their cost may be prohibitive. Fluidized-bed residues are collected dry, and appear to have a higher potential. Preliminary tests were conducted to determine the technical feasibility of using fluidized-bed residues in a mixture with emulsified asphalt. The results indicated that up to 92 percent of the aggregate could be replaced. Table 80 shows the approximate savings which could be realized assuming a free delivered price for the residues, and 92 percent replacement. For any given transport distance (or delivered price for residues) the net savings or costs per unit of asphalt can be easily calculated.

TABLE 80. IMPUTED VALUE OF RESIDUES IN ASPHALT APPLICATIONS

Item	Composition(%)		Value (\$/kkg) ^a		Cost Reduction (\$/kkg)
	Control	Residue Added	Control	Residue Added	
Asphalt Component					
Emulsified asphalt	8	8	94.53	94.53	0
Aggregate	92	0	4.96	0	4.96
Fly ash	0	92	0	b	0
Total	100	100	99.49	94.53	4.96

^aBased on a delivered cost (in Los Angeles) for asphalt of \$93.53/kkg and for aggregate of \$4.96.

^bValue of residue to be imputed from savings from its use.

Agriculture

Fluidized-bed residues can improve crop growth and yield by (1) altering pH (the residues are quite alkaline), (2) improving soil structure, (3) providing essential micronutrients (Zn, Cu, Fe, Mn, B, Cl, Al), (4) providing sulfur, and (5) serving as a source for macronutrients (O, C, H, N, P, K, Mg, Ca). Thus, the residues can serve many functions as an agricultural input. The purpose of this analysis is to estimate the value of the residues for agricultural applications. Because both the residues and many conventional agricultural inputs serve multiple functions, it is sometimes difficult to identify the inputs which, in a given application, could be replaced by fluidized-bed residues. Therefore, some of the analysis below will be based on the value of yield changes.

Research currently being conducted at the Virginia Polytechnic Institute and State University⁸⁴ has indicated that fluidized-bed residues can be used as a source of calcium for large-seeded peanuts, at least partially replacing application of calcium carbonate. The impact of providing a calcium source and a comparison between equal applications (980 kg/ha) of residue and calcium carbonate on yield were beneficial. On the average, both had a positive impact on yield, with the calcium carbonate increasing yield by 17 percent and the residue increasing it by 11 percent. However, at the given application rate, it is implied that the delivered price of residues would have to be significantly less than that for calcium carbonate to make up for the lower yield obtained. For example, the delivered price of calcium carbonate in Los Angeles, California, is about \$13.60 per kkg. Applying 980 kg to one hectare would cost \$13.33 for the material and result in (on the average) an extra \$84 of peanut production. Because the residues, as a source of calcium, are not as good as calcium carbonate on an equal weight basis, the farmer would have to be paid \$72.11/kkg to accept residues to make it economical for him to do so. Since this payment is unrealistic, use of residues in this application cannot be predicted on the basis of the field test results.

However, one factor, transporting costs, suggests that such application could be economically feasible. Although the calcium content of available calcium carbonate is about 40 percent, in comparison to the residues' approximate 10 percent, a higher residue application rate may result in matching yields achieved with calcium carbonate. For example, suppose 3,860 kg of residues per hectare could achieve the same yield as 980 kg of calcium carbonate per hectare (this would equalize calcium content). In this situation, the imputed value would be \$3.40 per kkg and, assuming the residues had a zero f.o.b. price at the power plant, the economically feasible transport distance would be 170 km by rail and 85 km by truck. This is, of course, a hypothetical result and more experimental work needs to be completed before the economic feasibility of this application can be determined.

Test pilot D in Table 81 shows an improvement in yield for the spent bed material versus the calcium carbonate. As discussed above, the residues may fulfill several functions in plant growth. Apparently in Plot D, a growth requirement is being met by the residues

which calcium carbonate does not meet. The value (relative to calcium carbonate) in this application is \$250 for increased yield and \$13 saved by replacing calcium carbonate, for a total value of \$263 per 980 kg. This represents an imputed value for the spent-bed material of \$268 per kkg. However, there would likely be other inputs capable of filling the same need, and the proper comparison would be without that input. There is some evidence that in certain types of soil the fluidized-bed residues will achieve higher yields than will ordinary limestone, even at equal application rates. The VPI study identified "Woodstock loamy fine sand" as possibly being such a soil type.

TABLE 81. FLUIDIZED - BED RESIDUES AS A SUBSTITUTE FOR CALCIUM CARBONATE IN PEANUT GROWING

Material Applied	Application Rate (kg/ha)	Yield (\$/ha)					
		A	B	C	D	E	Avg
Control	0	1190	1097	1907	1225	1862	1457
Calcium carbonate	980	1420	1337	2109	1489	1894	1699
Spent bed material	980	1317	1151	2040	1739	1830	1615

Source: 84.

Fluidized-bed ash and spent bed material are both quite alkaline and hence can be used to raise soil pH. In that function, it is a substitute for slaked lime ($\text{Ca}(\text{OH})_2$). The delivered price of slaked lime in Los Angeles is approximately \$65 per kkg. The amount of NJFA necessary to cause the same pH adjustment as the slaked lime has been estimated to be 13.5 kg; for NJSBM the equivalent is 5.5 kg. This corresponds to an imputed value for NJFA of \$4.80 per kkg and for NJSBM of \$11.80 per kkg. Again, assuming a zero f.o.b. price at the power plant, the NJFA residues could be economically transported 240 km, and the NJSBM residues 590 km by rail. It should be stressed, however, that these calculations assume that the only function provided by either the residues or the slaked lime is pH adjustment. Since this is not the case, it would be necessary to know the yield response for different types of soils and plants to draw firm conclusions on the economic feasibility of this application. Each conclusion would be specific for a given type of crop and soil condition.

The market for pH adjustment materials is quite large. On an average, 675-900 kg/ha/year of limestone is needed to maintain optimal soil pH in areas where large quantities of nitrogen

fertilizers are used. For several reasons, one of which is the expense of limestone, less limestone is used than is necessary for optimal yields. It has been estimated that in the United States, about 80-90 million kkg of limestone could be used annually to advantage.¹² In those areas where the delivered price of residues is significantly less than for limestone, on an equivalent basis it can be expected that farmers would more nearly approach the optimal level of application. The potential market for the residues is therefore substantially greater than our projected generation rate of 2 to 12 million kkg per year for 1995. As discussed previously, however, there are also substantial impediments to large-scale utilization for this purpose, such as transportation costs and the need for farmer education.

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APPENDIX A

LABORATORY ANALYTICAL METHODS

Chemical analyses were performed on leachate from the laboratory-scale columns, the pilot scale columns, and test cells. Environmental Protection Agency methods (Manual of Methods for Chemical Analysis of Water and Wastes, EPA 625/6-74-003) were used for all analyses. The analyses performed, the methods used, and references for the methods are shown in Tables A-1 and A-2.

To insure the validity of the test results, EPA-approved quality control procedures were instituted. The program involved co-analysis of a series of standards, duplicate unknowns, and spiked unknowns. One duplicate was run for every four samples; where there were fewer than four samples, all were duplicated. Spikes were run on one of every eight samples; for fewer than eight samples, at least one spike was run. Standards were scattered throughout the runs to maintain instrument calibration. All reagents were checked for stability on a rotating basis which covered each reagent at least twice yearly.

TABLE A-1. SOIL PREPARATORY METHODS

Purpose	Method	Reference ^a (page number)
Total Residue Characterization	Hydrofluoric and perchloric acid digestion	1019
Soluble Fraction Analyses	Water extraction	935
	Acid extraction (1.0 N <u>nitric acid</u>)	935 ^b
	Base extraction (1.0 N <u>sodium hydroxide</u>)	935 ^c
Cation Exchange Capacity	Sodium saturation	899
Tomato Plant Analyses	Wet digestion	11 ^d

^a American Society of Agronomy. Methods of Soil Analysis, Part 2, Madison, Wisconsin; 1965; except as noted.

^b Same as water extraction, except nitric acid solution was substituted for distilled water.

^c Same as water extraction, except sodium hydroxide solution was substituted for distilled water.

^d Sub-committee of NC-118. Sampling and Analysis of Soils, Plants, Waste Waters, and Sludge. Research Publication 170, Agricultural Experiment Station, Kansas State University, Manhattan, Kansas.

TABLE A-2. ANALYTICAL METHODS

Parameter	Performed on				Method	Reference ^e (page number)
	RC ^a	LCL ^b	PCL ^c	PD ^d		
Metals						
Aluminum	X				Colorimetric (Eriochrome cyanide R)	92
Arsenic		X			Colorimetric (Silver diethyldithiocarbamate)	9
Beryllium	X				Atomic Absorption	99
Cadmium	X	X			Atomic Absorption	101
Calcium	X	X			Flame Emission	103
Chromium	X				Atomic Absorption	105
Copper	X				Atomic Absorption	108
Iron	X	X	X	X	Atomic Absorption	110
Lead	X	X	X		Atomic Absorption	112
Magnesium	X	X		X	Atomic Absorption	114
Manganese	X	X	X	X	Atomic Absorption	116
Mercury	X	X	X		Flameless Atomic Absorption	118
Nickel	X	X	X		Atomic Absorption	141
Potassium	X	X			Flame Emission	143
Silver	X	X	X		Atomic Absorption	146
Sodium	X	X			Flame Emission	147
Zinc	X	X	X	X	Atomic Absorption	155
Physical						
Total Dissolved Solids	X		X		Gravimetric	267
Specific Conductance			X		Electrometric (platinum electrode)	275
Inorganic						
Boron	X	X			Colorimetric (Curcumin)	13
Chloride	X	X	X		Titrimetric (Mercuric nitrate)	29
Nitrate	X	X			Colorimetric (Brucine)	197
pH	X	X	X	X ^f	Electrometric	239
Phosphate	X				Colorimetric (Ascorbic Acid)	481 ^g
Sulfate	X	X	X	X	Turbidimetric	277
Organic						
BOD	X	X			Manometric	1558 ^h
COD	X		X		Dichromate reflux	
			X		Low Levels	21
					High Levels for Saline Samples	25

(continued)

TABLE A-2 (continued)

- ^a RC - Residue characterization.
- ^b LCL - Lab column leachate.
- ^c PCL - Pilot column leachate.
- ^d PD - Plant digested sample.
- ^e U. S. Environmental Protection Agency. Manual of Methods for Chemical Analysis of Water and Wastes. EPA-625/6-74-003. Washington, D. C. Office of Technology Transfer, US EPA, 1974.
- ^f Analyzed on 1:1 plant/distilled water mixture.
- ^g American Public Health Association, Standard Methods, 14th ed., Washington, D. C., 1976.
- ^h American Society of Agronomy. Methods of Soil Analysis, Part 2. Madison, Wisconsin, 1965.

APPENDIX B
SAMPLE DATA SHEET

SURVEY OF PILOT PLANTS USING FLUIDIZED BEDS FOR THE COMBUSTION OF
COAL AND THE GASIFICATION OF HIGH-SULFUR FUEL OILS

We are conducting special studies for the U.S. EPA (Contract No. 68-03-2347; Project Officer, Richard Chapman: 1346 Willow Road, Menlo Park, California 94025) on the residues from the fluidized bed combustion of coal and the gasification of high-sulfur fuel oils. The purpose of this questionnaire is to provide us with basic design information on the pilot plants covered by the study to aid in our assessment of residue disposal impacts. Please complete and return to:

Ralph Stone and Company, Inc.
10954 Santa Monica Boulevard
Los Angeles, California 90025 USA
Phone: (213) 478-1501 and 879-1115

1. General Pilot Plant Characteristics

a. Name of plant: _____

b. Address: _____

c. Designer: _____

Address: _____

d. Operating organization: _____

2. Construction Information

a. General contractor: _____

b. Construction commencement date: _____

c. Construction completion date: _____

d. Start-up date: _____

e. Total capital cost: _____

3. General Information

a. Number of employees required to operate pilot plant: _____

b. Number of operating days in 1975: _____

c. Number of days shut down for maintenance, process modification, etc.: _____

d. Estimated annual operating cost: _____

4. Operating Information. Please give design estimates rather than actual operating values. Answer in listed units of measure, if possible; if other units are used, please specify them.

a. Bed volume (cu m): _____

b. Quantity of bed material (kg): _____

c. Average bed material feed rate (kg/min): _____

d. Average particle size of bed material (cm): _____

e. Mode of operation

(1) Number of stages: _____

(2) () Batch; () continuous (check one)

(3) () Once through; () regenerated (check one)

f. Coal or oil feed rate (kg/hr): _____

g. Air requirements (scfm): _____

h. Fuel hydrogen requirements (scfm): _____

i. Combustion efficiency: _____

j. Power output (kwhr): _____

k. Heat released (Btu/hr): _____

l. Please describe number and types of flue gas control equipment (cyclones, scrubbers, etc.).

m. Quantities and types of wastes produced.

solid:

fly ash: _____

spent bed material: _____

liquid:

type: _____; quantity: _____

type: _____; quantity: _____

4. Operating Information (cont.)

n. Describe handling and storage facilities used for the different kinds of wastes.

[illegible]

5. Please provide a copy of the results of any analyses which have been conducted on the spent bed material and fly ash and copies of recent progress or other reports.

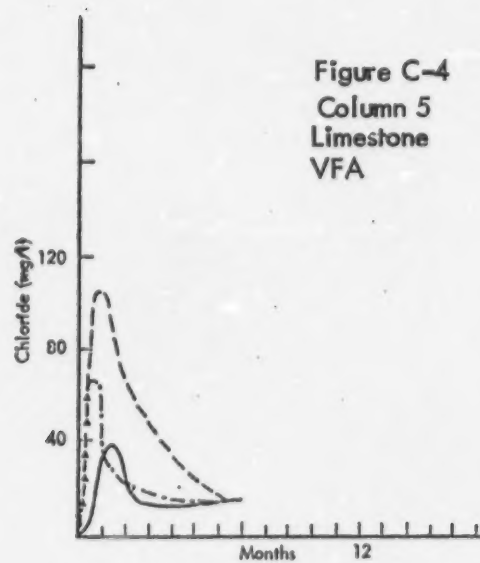
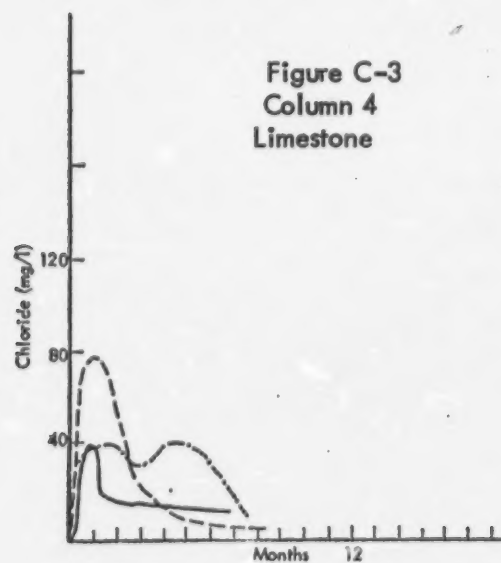
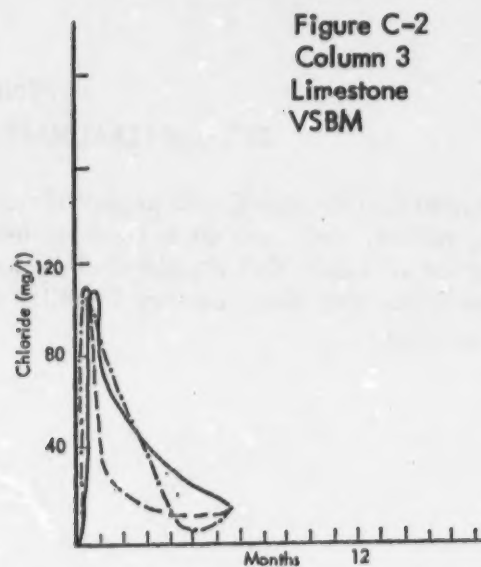
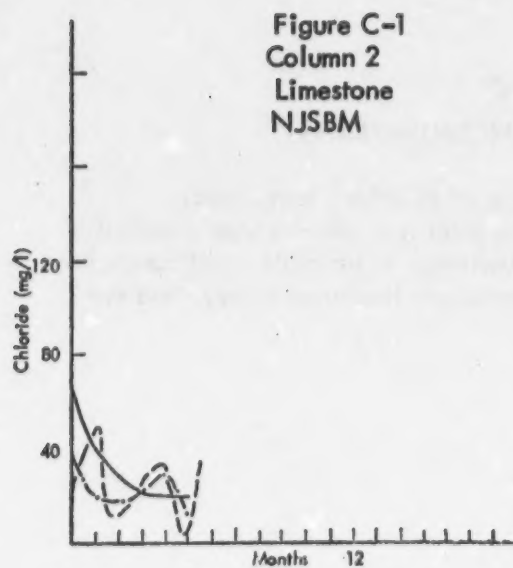
Use the space below or an additional page for additional comments.

Thank you for your generous cooperation.

APPENDIX C

COLUMN LEACHATE CONCENTRATIONS

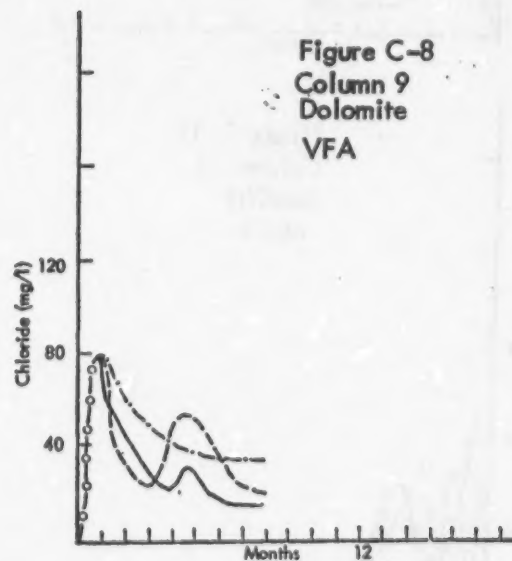
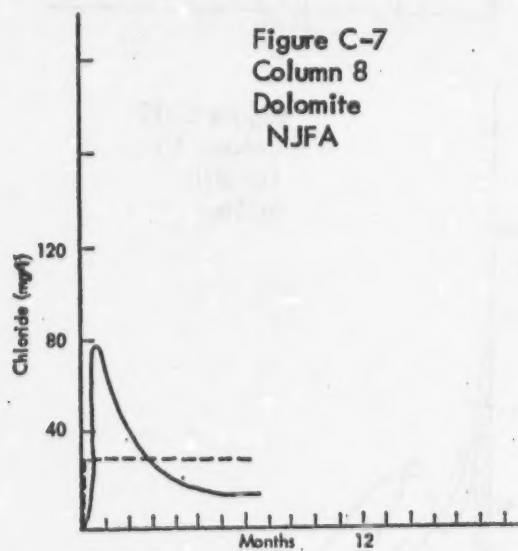
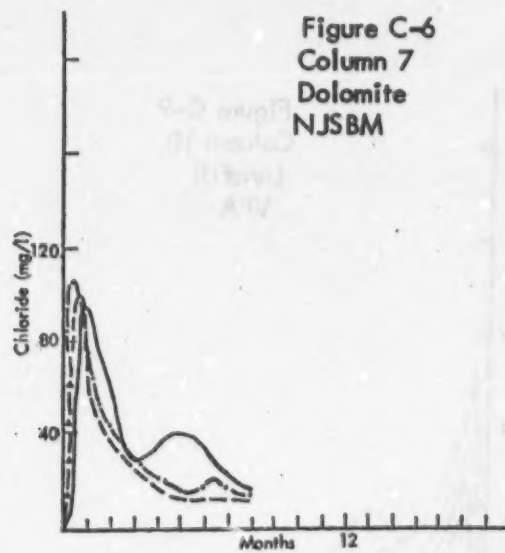
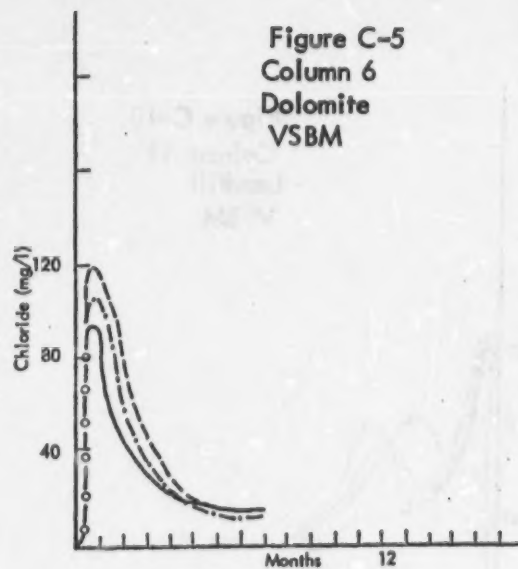
Figures C-1 through C-130 present the amounts of chloride, iron, lead, nickel, sulfate, zinc, and pH of leachate from the pilot test columns over a period of eight months. Tables C-1 through C-5 show the variation in leachate constituents from residues in the coal mine, sanitary landfill, dolomite and limestone quarry, and sea water columns.



Legend

Top lysimeter	-----
Bottom lysimeter	
Top and bottom lysimeters	-----▲-----
Drain	—————

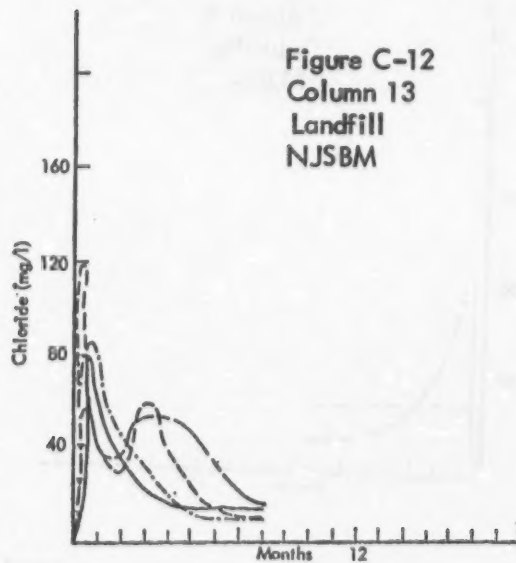
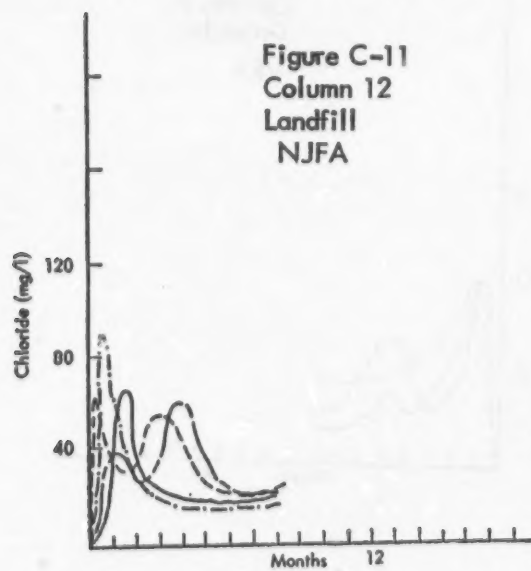
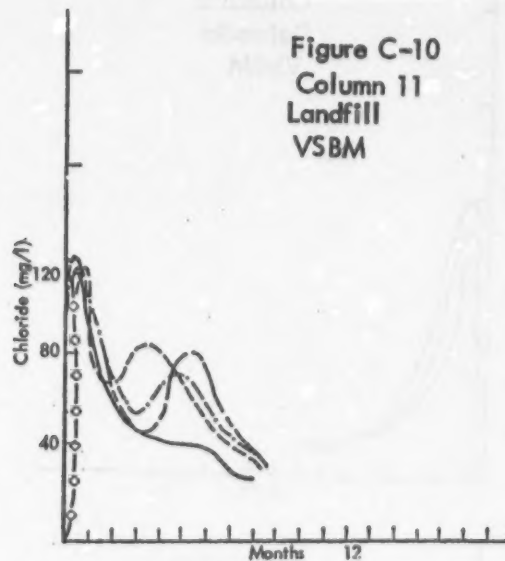
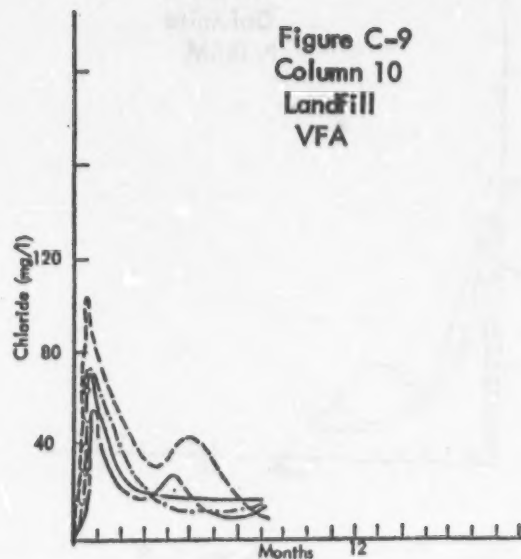
Figures C-1 - C-4. Chloride leachate from Columns 2 to 5. Limestone quarry.



Legend

Top lysimeter	---
Bottom lysimeter	-.-.-
Drain	—
Drain and top and bottom lysimeters	—○—○—
Top and bottom lysimeters	—△—△—

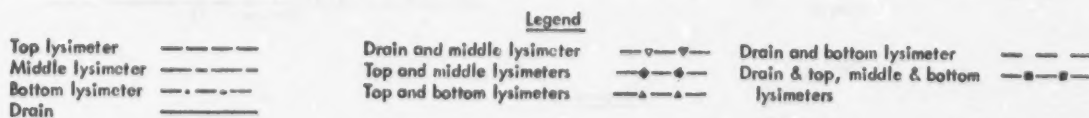
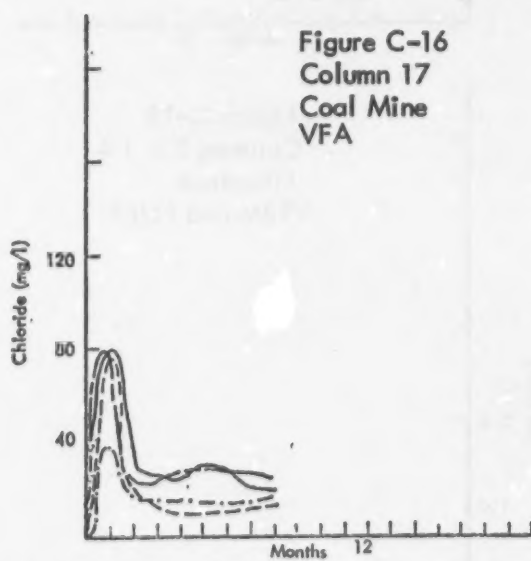
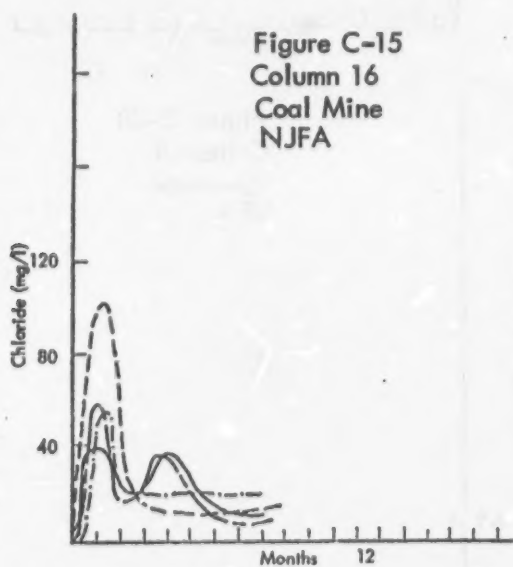
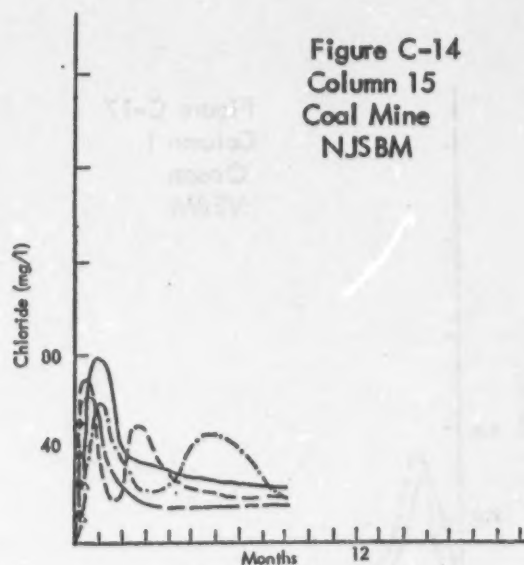
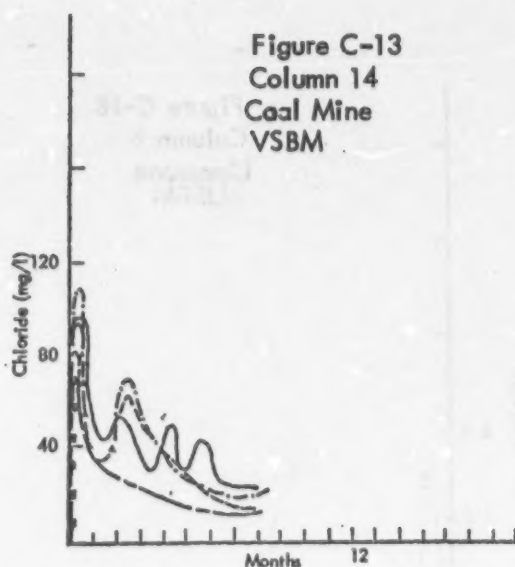
Figures C-5 - C-8. Chloride leached from Columns 6-9: Dolomite quarry.



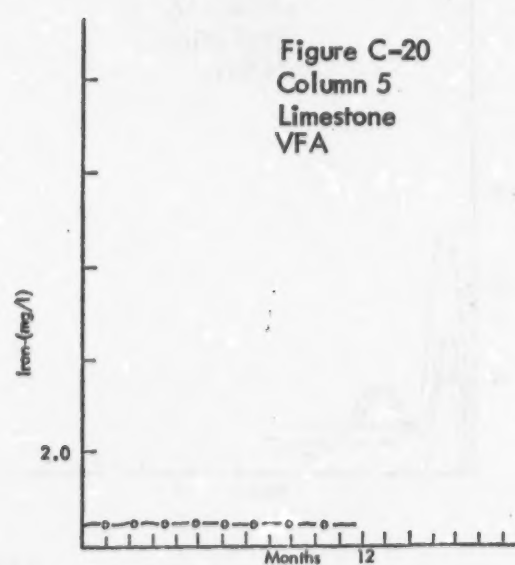
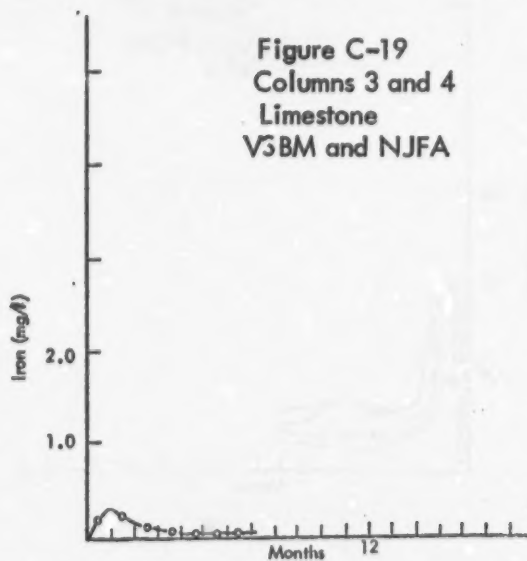
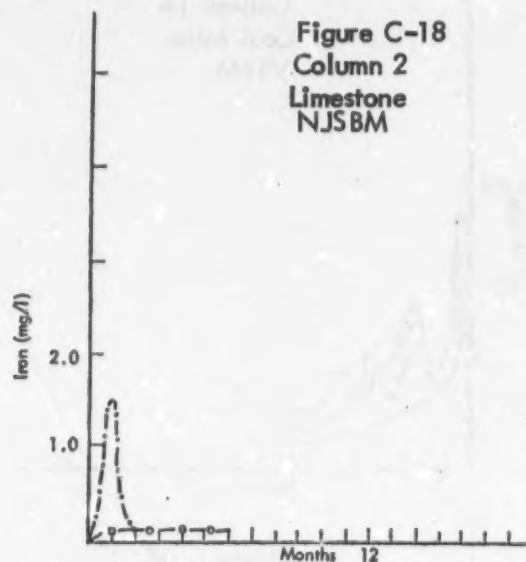
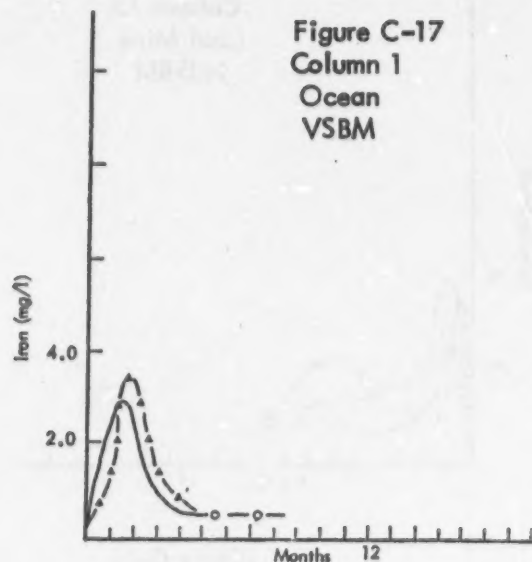
Legend

Top lysimeter	---	Top, middle, and bottom lysimeters	—▼—▼—
Middle lysimeter	—	Drain and top and middle lysimeters	—○—○—
Bottom lysimeter	...	Drain and middle lysimeters	—▼—▼—
Drain	-.-		

Figures C-9 - C-12. Chloride leached from Columns 10 to 13. Sanitary landfill.



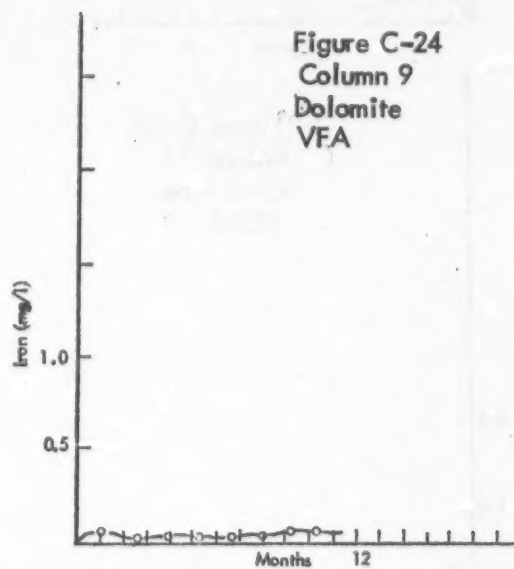
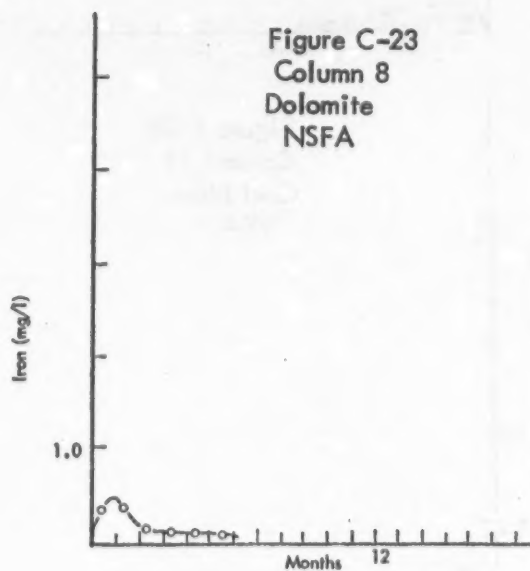
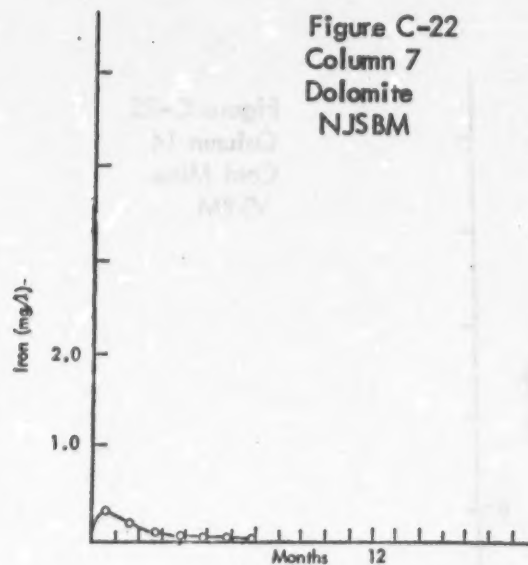
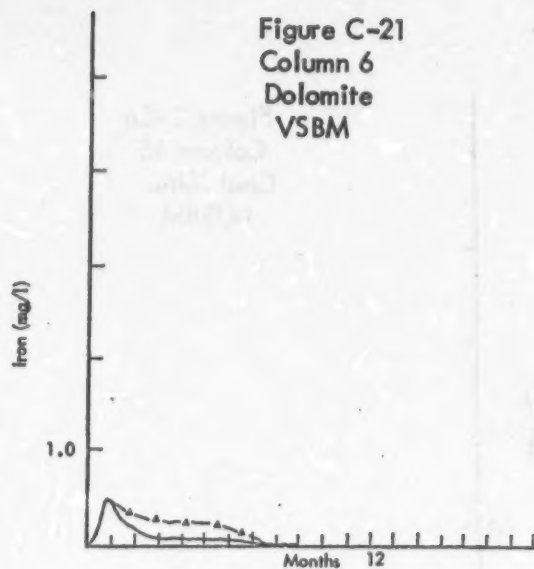
Figures C-13 - C-16. Chloride leached from Columns 14 - 17; Coal mine.



Legend

Bottom lysimeter	---○---○---
Drain and top lysimeters	---□---□---
Top and bottom lysimeters	---△---△---
Drain and top and bottom lysimeters	-----

Figures C-17 - C-20. Iron leached from Columns 1 to 5: Ocean and Limestone quarry.



Legend

Top and bottom lysimeters

Drain

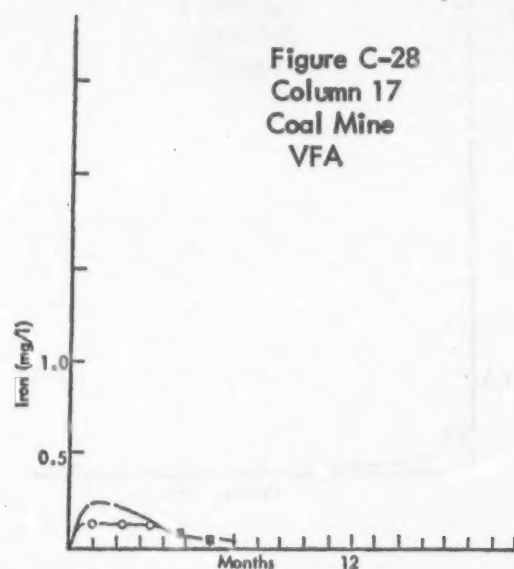
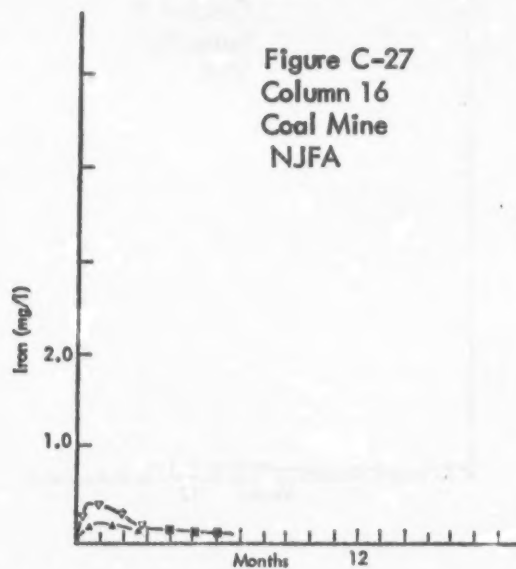
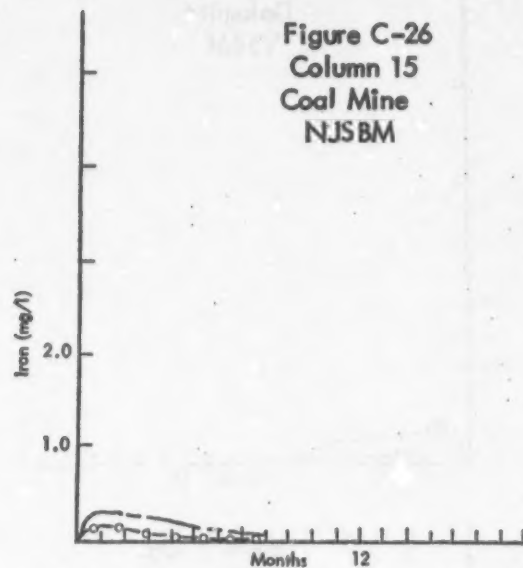
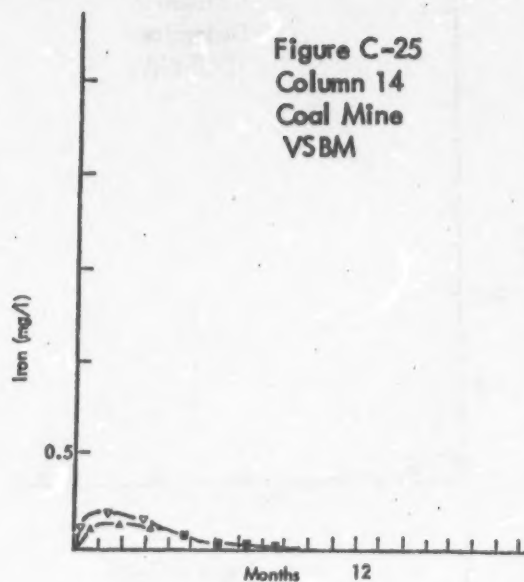
Drain & top & bottom lysimeters

—▲—▲—

————

—○—○—

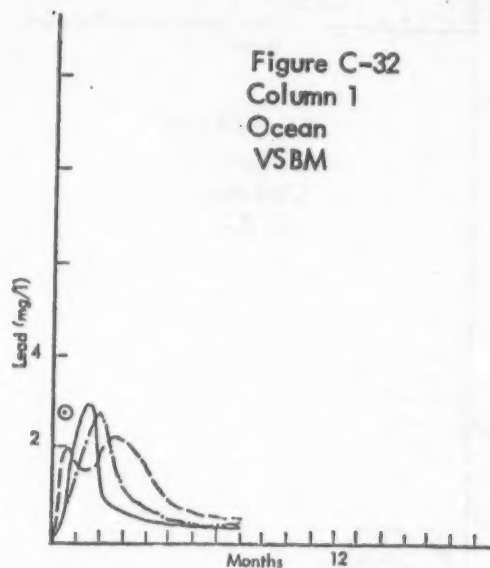
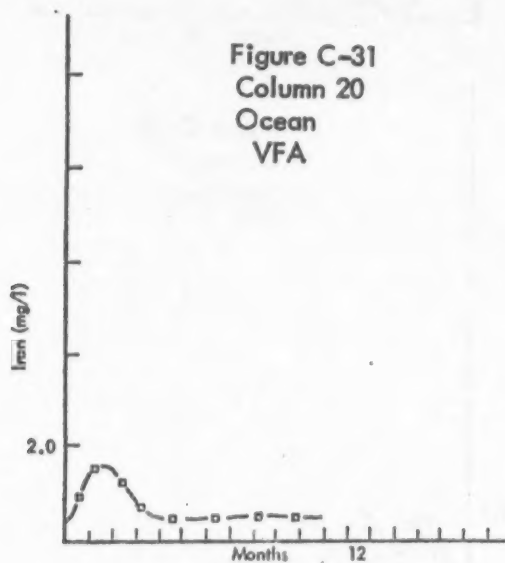
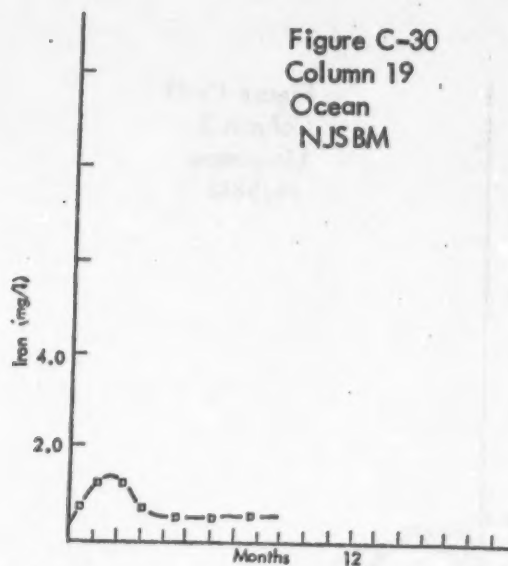
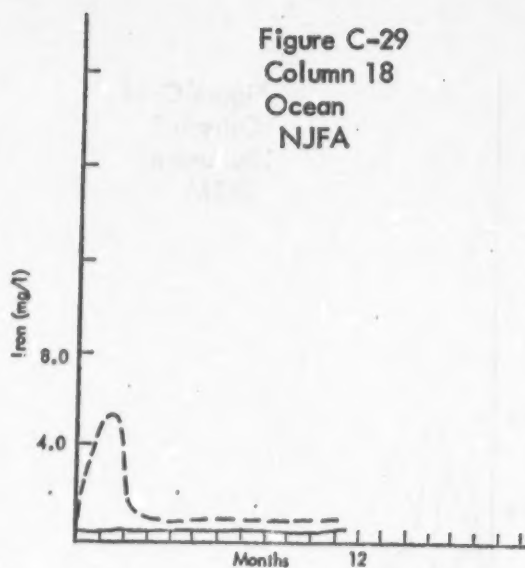
Figures C-21 - C-24. Iron leached from Columns 6 to 9. Dolomite quarry.



Legend

Middle lysimeter	-----
Drain & top & bottom lysimeters	—○—○—
Drain and middle lysimeter	—v—v—
Top and bottom lysimeter	—△—△—
Drain, top, middle & bottom lysimeters	—■—■—

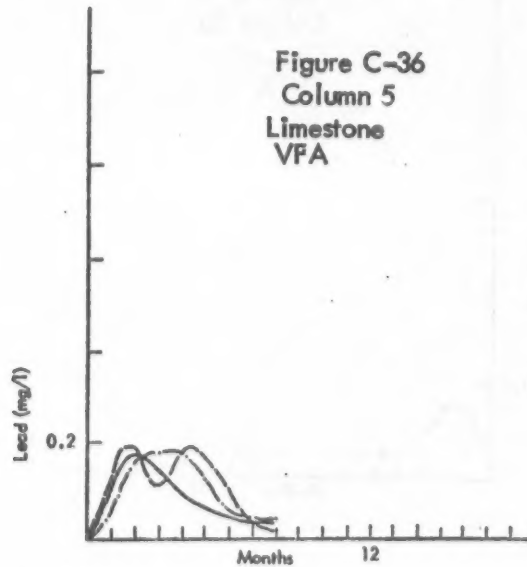
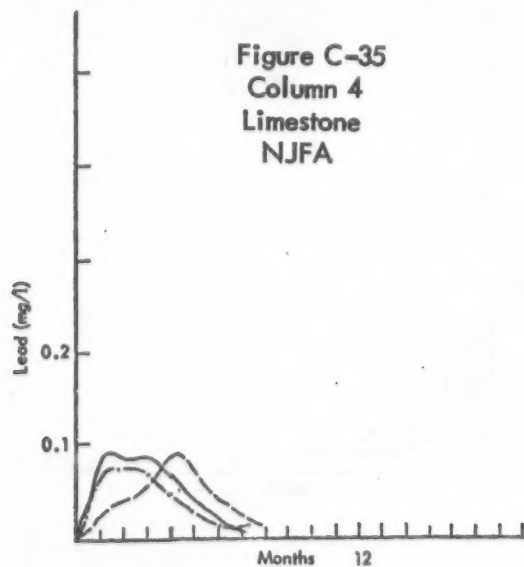
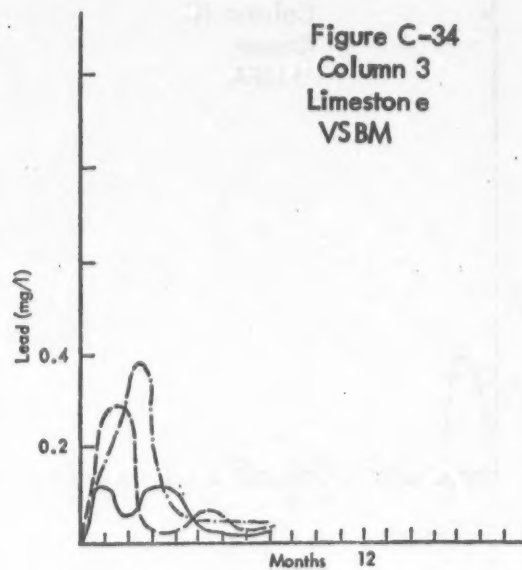
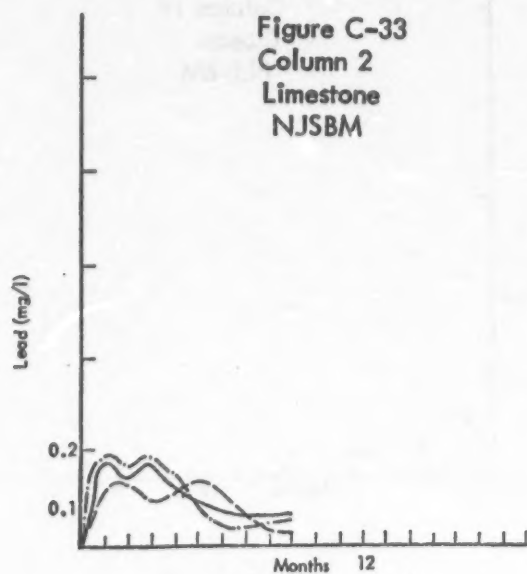
Figures C-25 - C-28. Iron leached from Columns 14 to 17: Coal mine.



Legend

Drain	————
Bottom lysimeter	- . - . -
Top lysimeter	- - - - -
Drain and top lysimeter	- □ - □ -
Incoming water	⊙

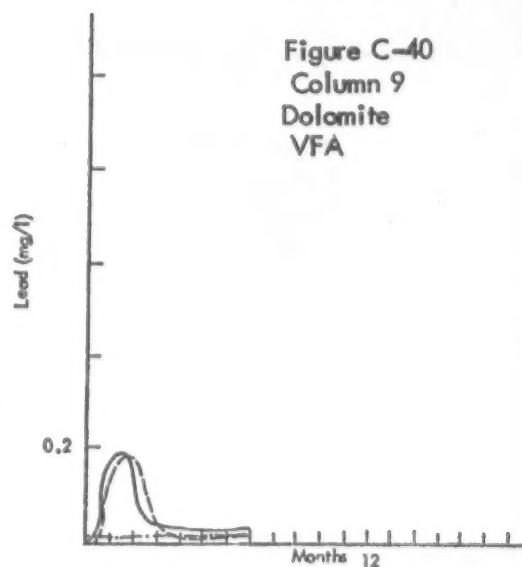
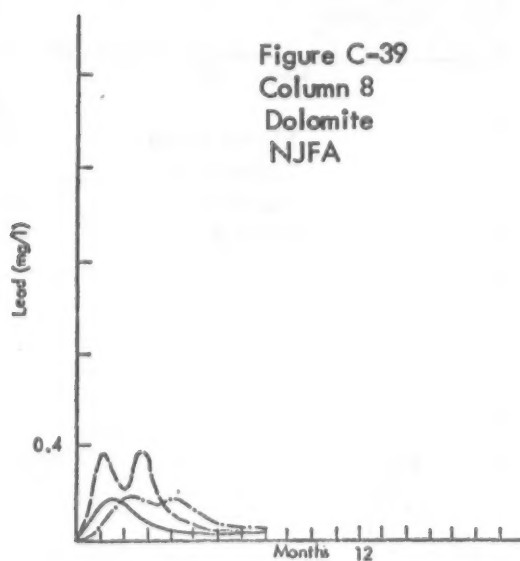
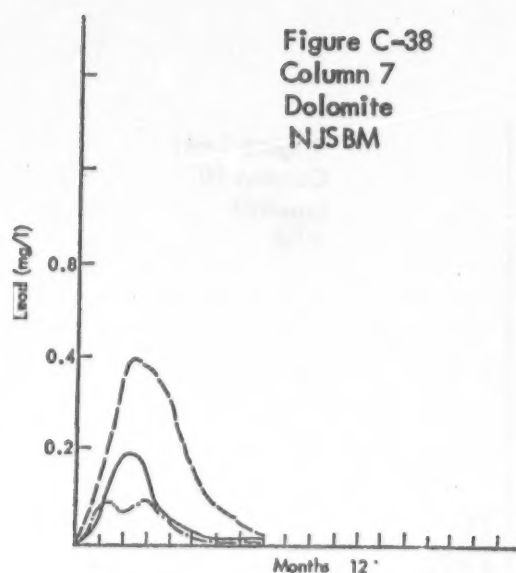
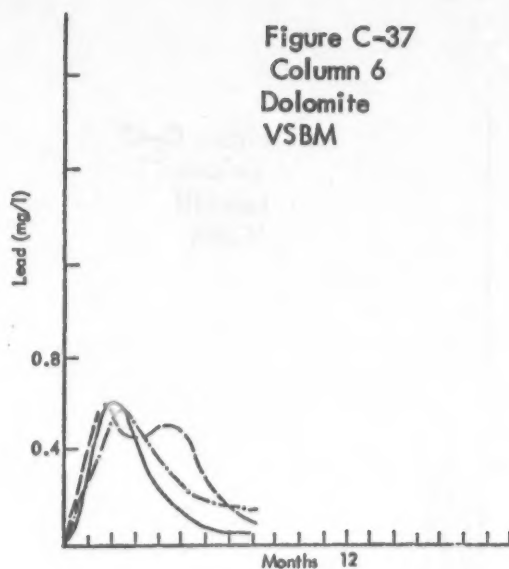
Figures C-29 - C-32. Iron and lead leached from Columns 18 to 20 & 1: Ocean.



Legend

Top lysimeter	----
Bottom lysimeter	- . - . -
Drain	_____

Figures C-33 - C-36. Lead leached from Columns 2 to 5: Limestone quarry.



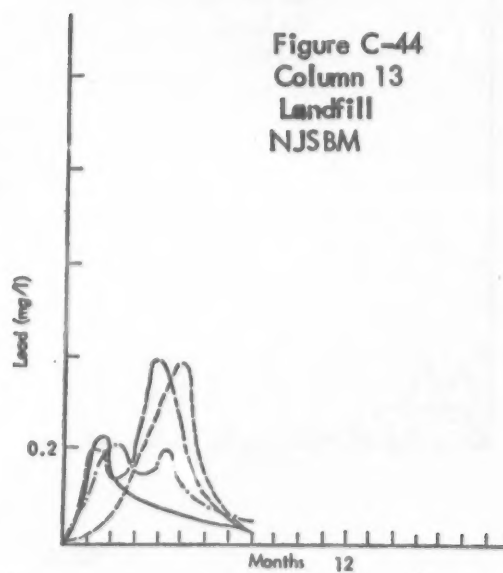
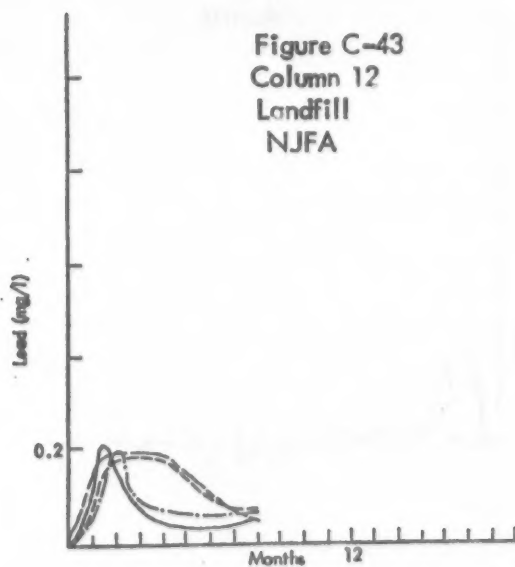
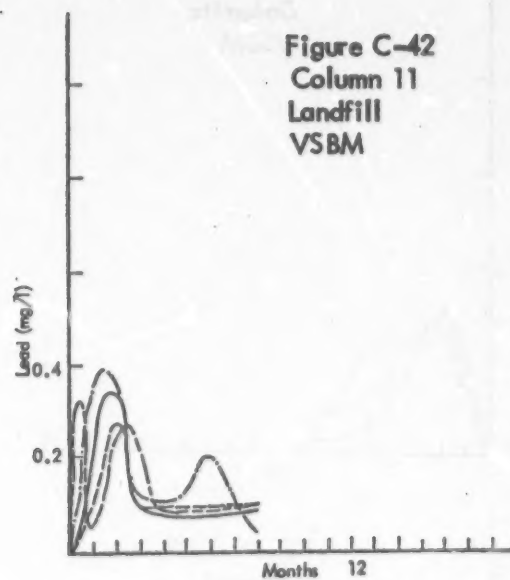
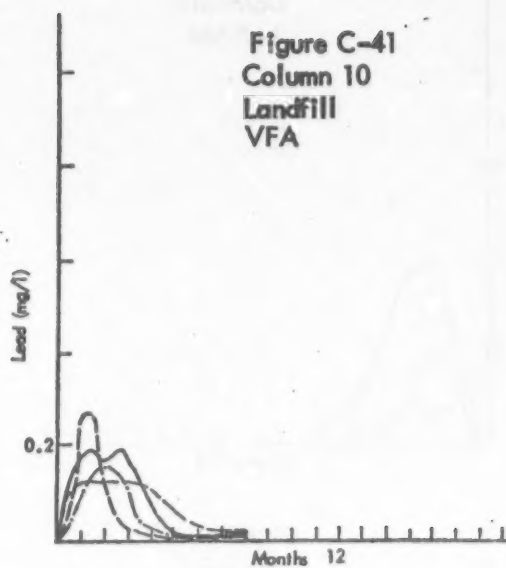
Legend

Top lysimeter -----

Bottom lysimeter - . - . -

Drain _____

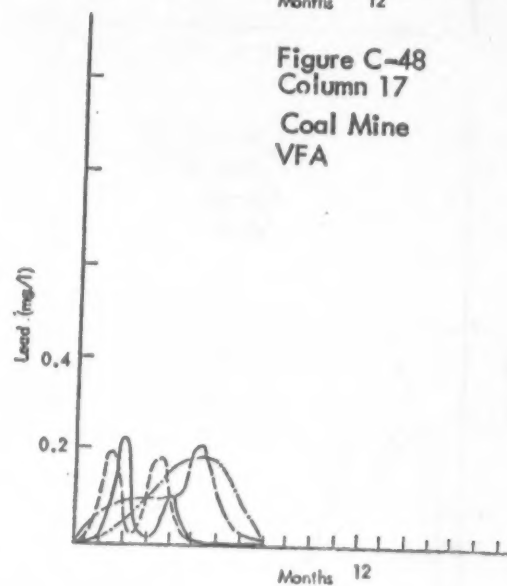
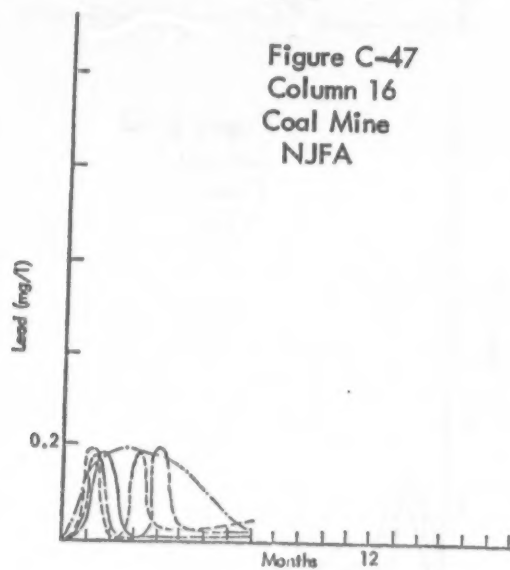
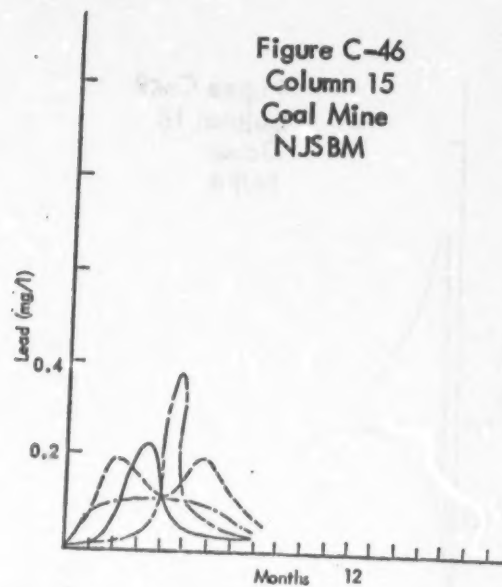
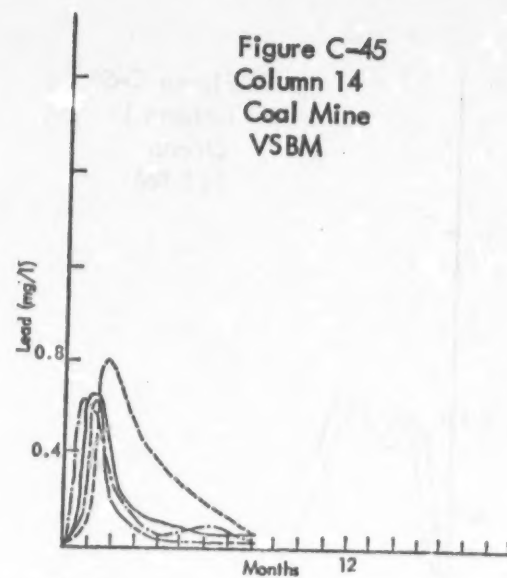
Figures C-37 - C-40. Lead leached from Columns 6 to 9; Dolomite quarry.



Legend

Top lysimeter	----
Middle lysimeter	
Bottom lysimeter	-.-.-.-
Drain	————

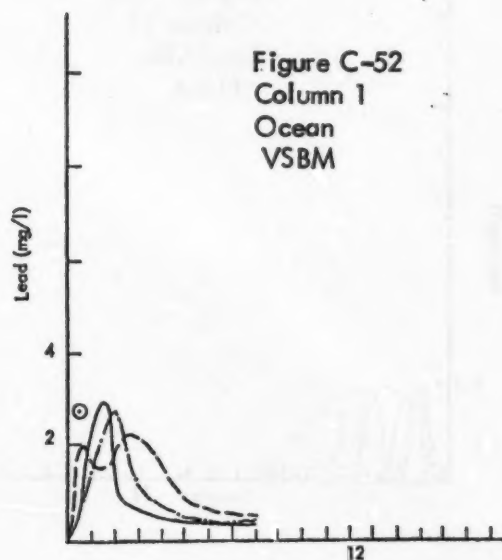
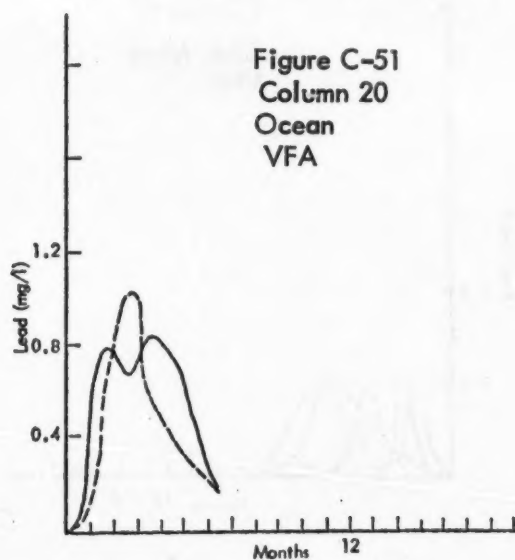
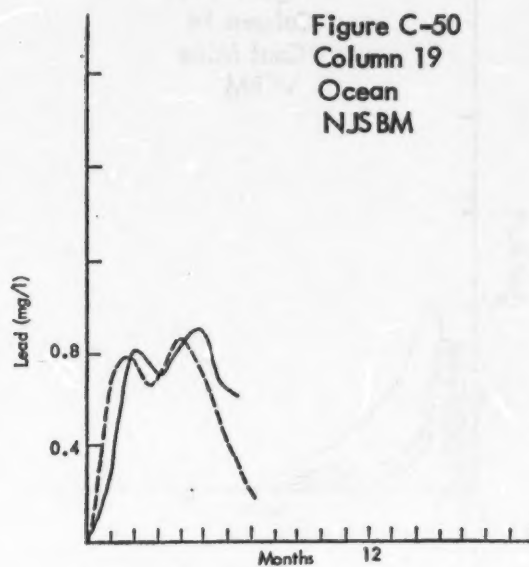
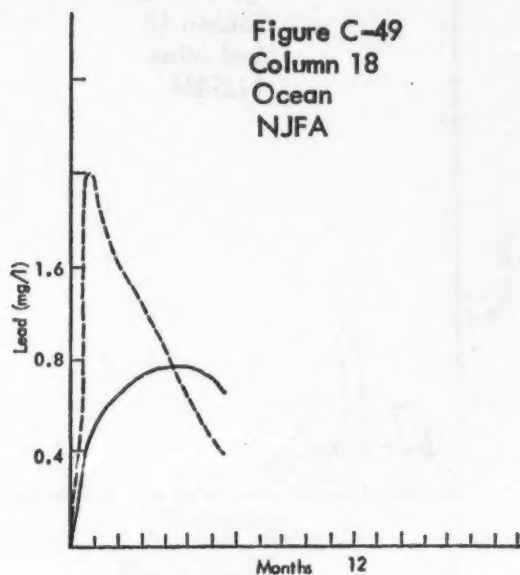
Figures C-41 - C-44. Lead leached from Columns 10 to 13. Sanitary landfill.



Legend

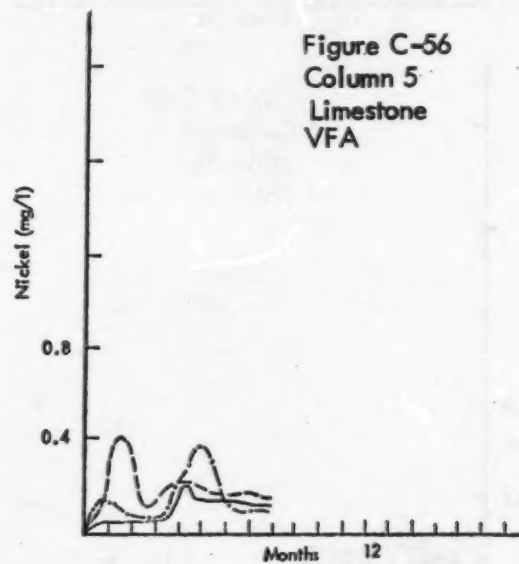
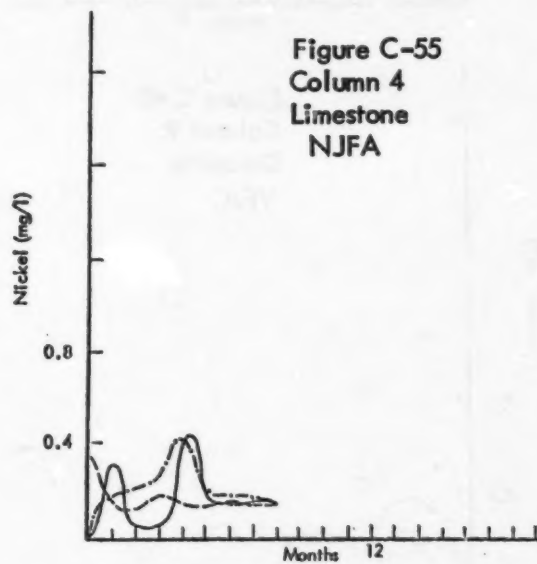
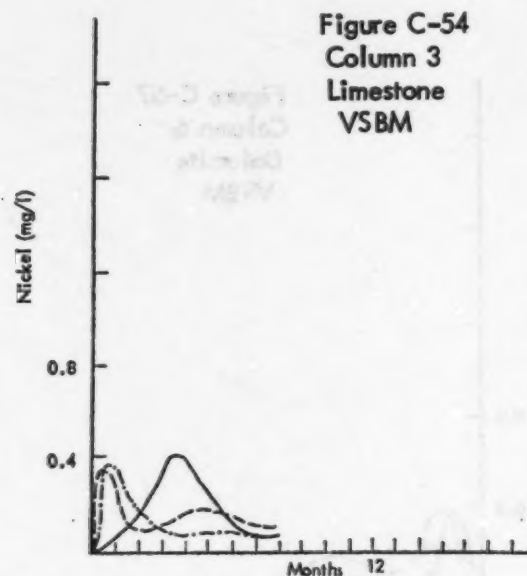
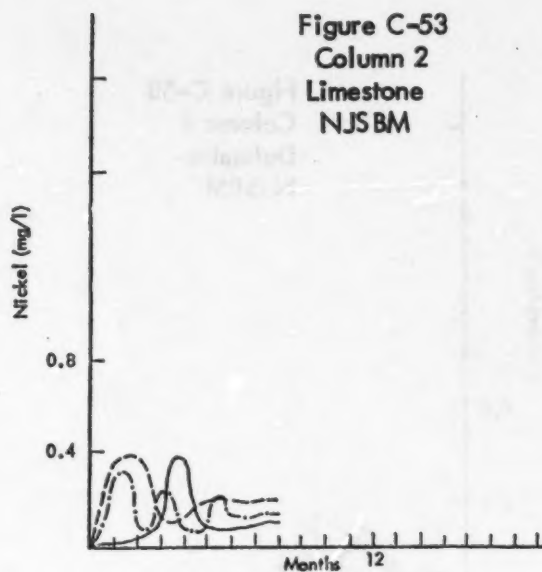
Top lysimeter	----
Middle lysimeter	- - - -
Bottom lysimeter	- . - .
Drain	_____

Figures C-45 - C-48. Lead leached from Columns 14 to 17: Coal Mine.



Legend
Top lysimeter - - - - -
Bottom lysimeter - . - . -
Drain ———

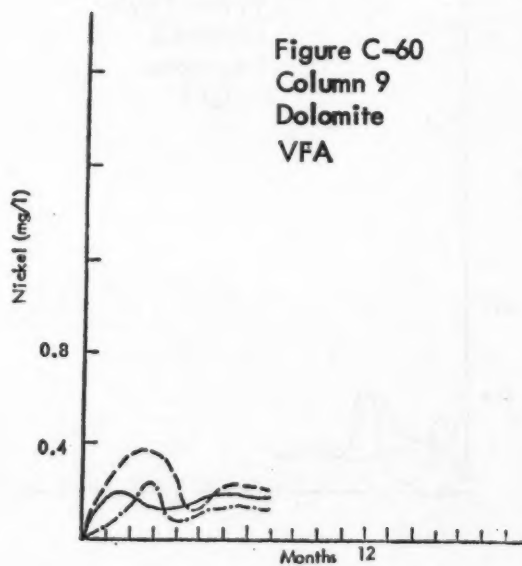
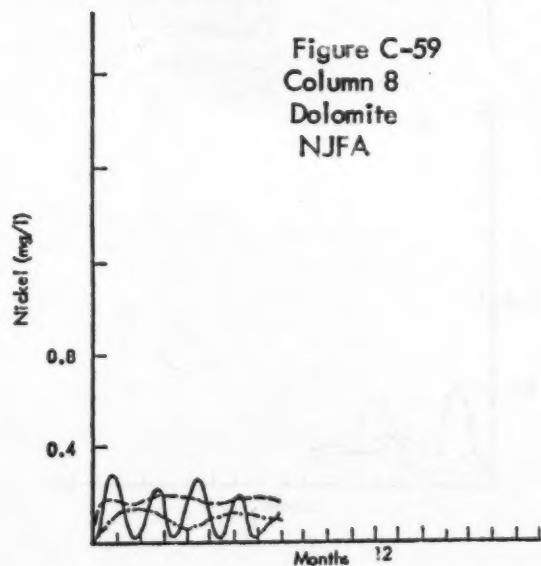
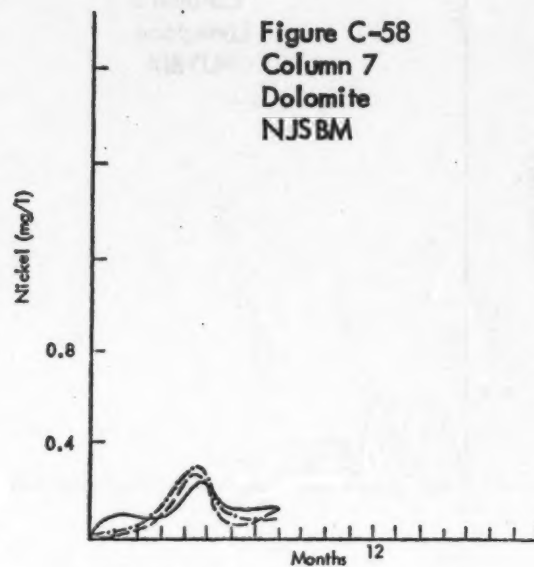
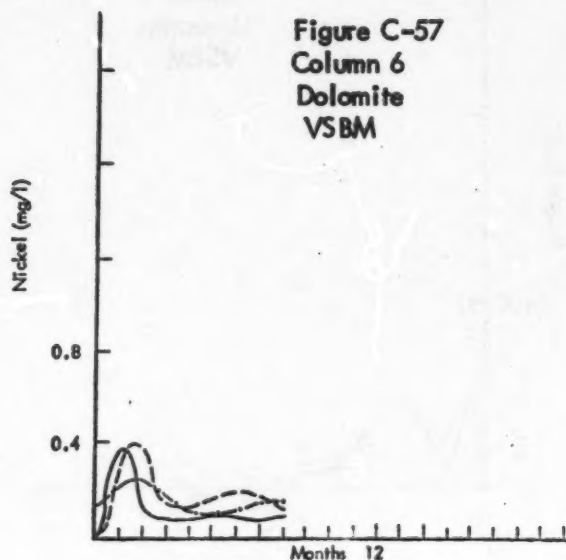
Figures C-49 - C-52. Lead leached from Columns 18 to 20 and 1: Ocean.



Legend

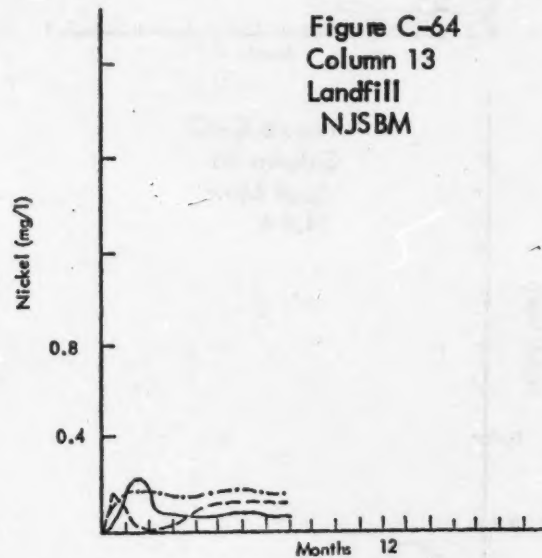
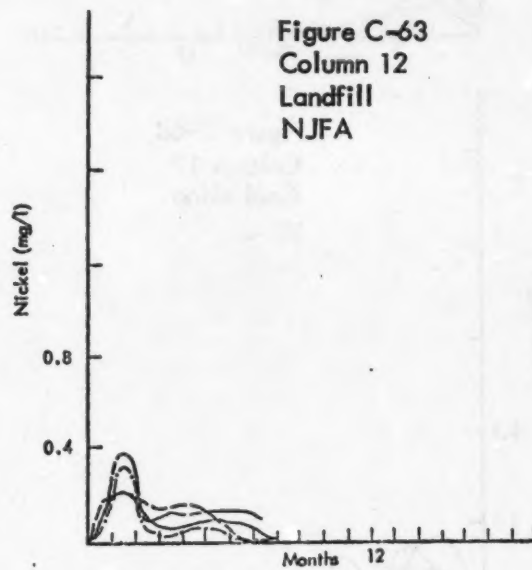
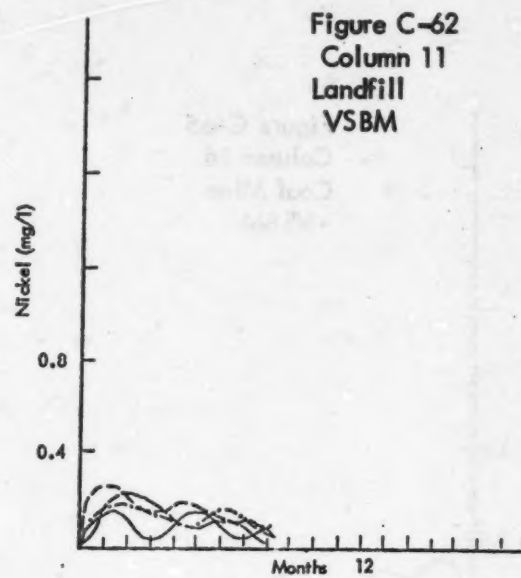
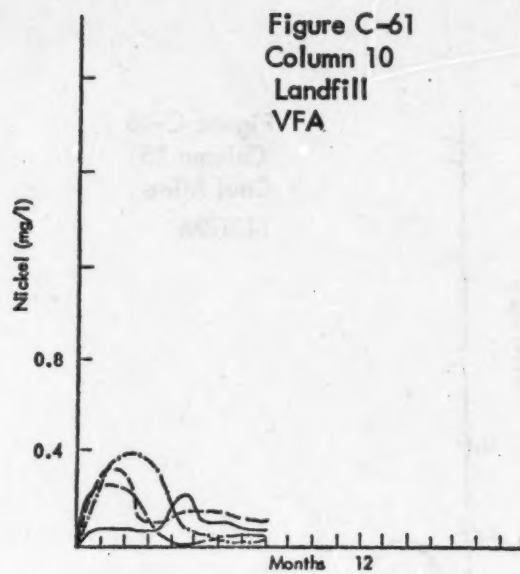
Top lysimeter	----
Bottom lysimeter	
Drain	_____

Figures C-53 - C-56. Nickel leached from Columns 2 to 5: Limestone quarry.



Legend
Top lysimeter ---
Bottom lysimeter - - -
Drain - . -

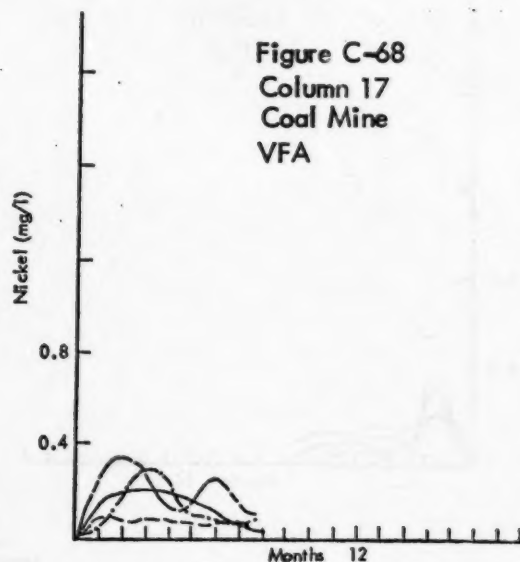
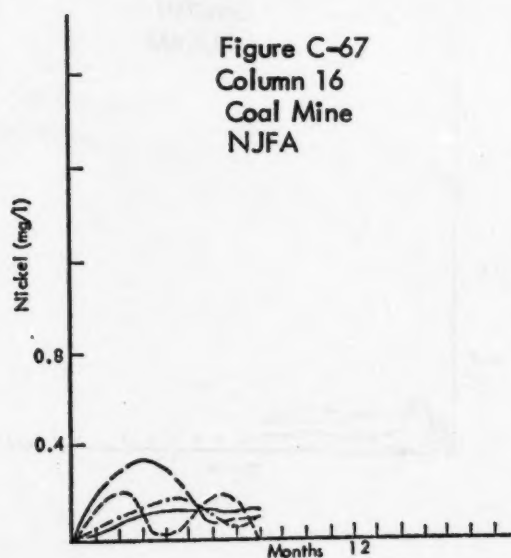
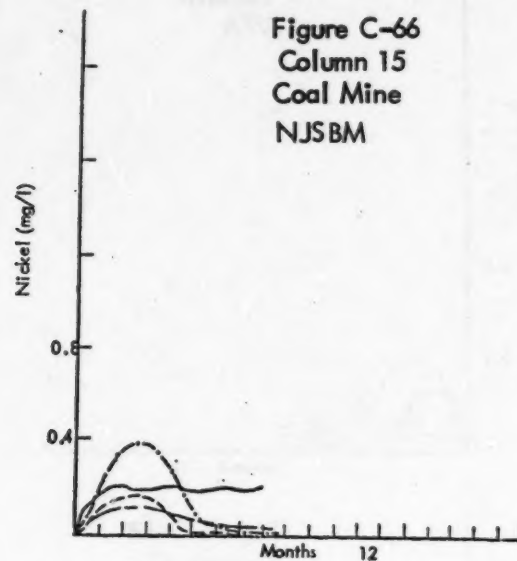
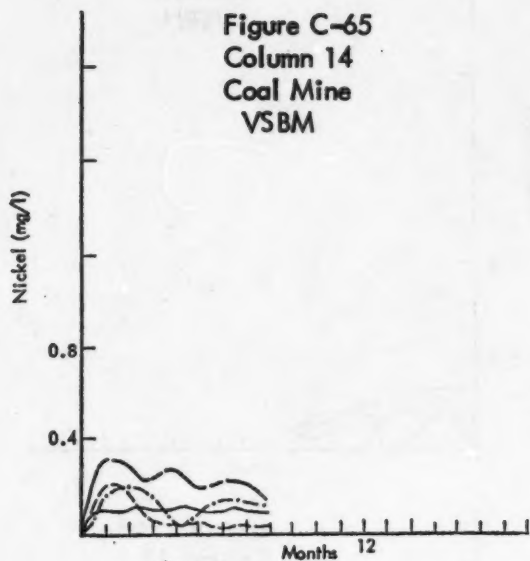
Figures C-57 - C-60. Nickel leached from columns 6 to 9. Dolomite quarry.



Legend

Top lysimeter	-----
Middle lysimeter	————
Bottom lysimeter	—•••—
Drain	————

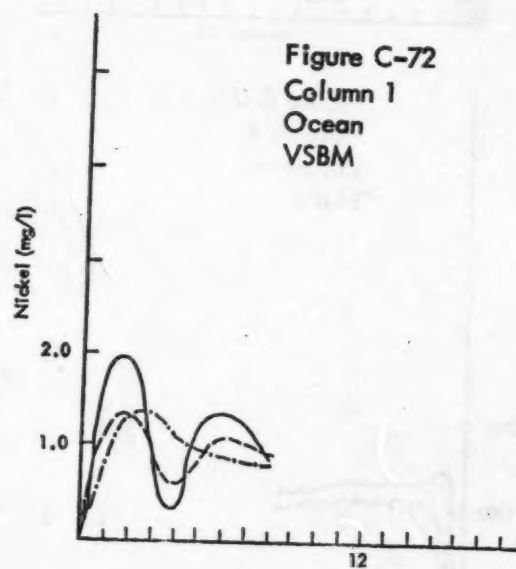
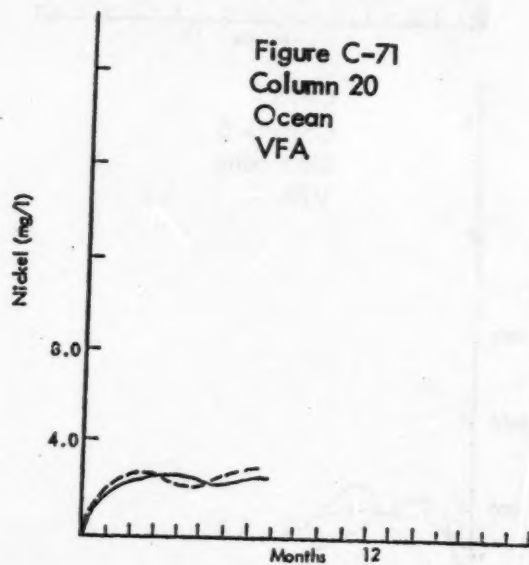
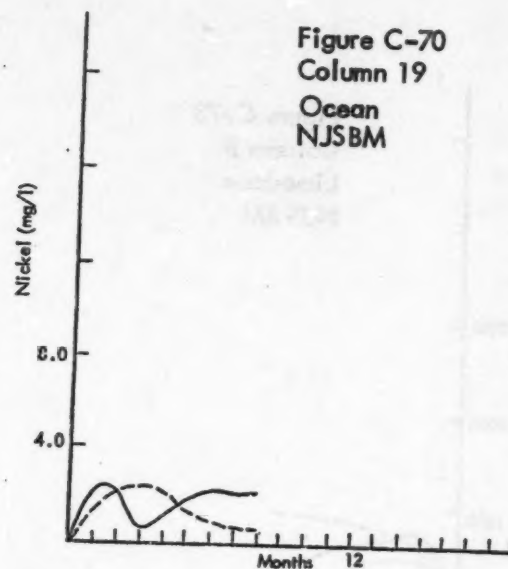
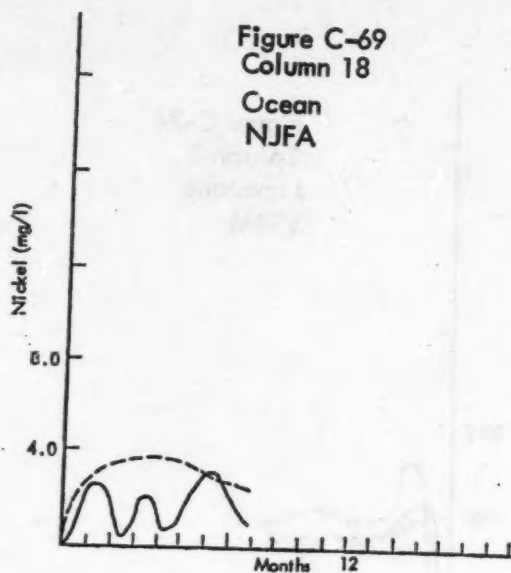
Figure C-61 - C-64. Nickel leached from Columns 10 to 13: Sanitary landfill.



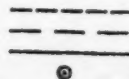
Legend

Top lysimeter	----
Middle lysimeter	_____
Bottom lysimeter	
Drain	=====

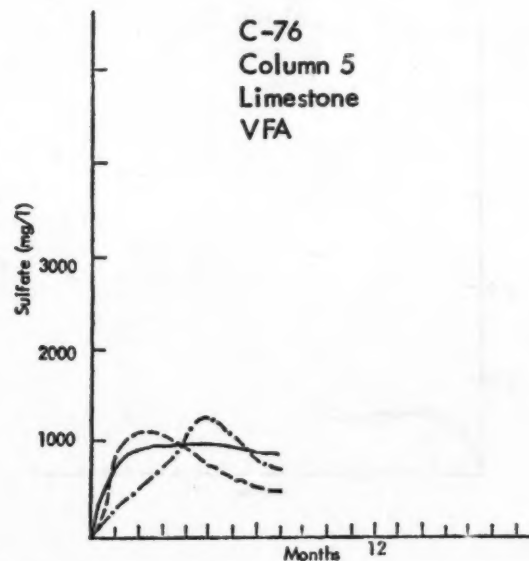
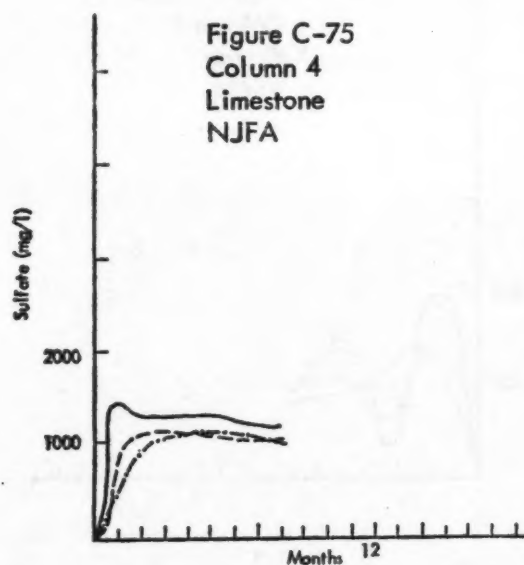
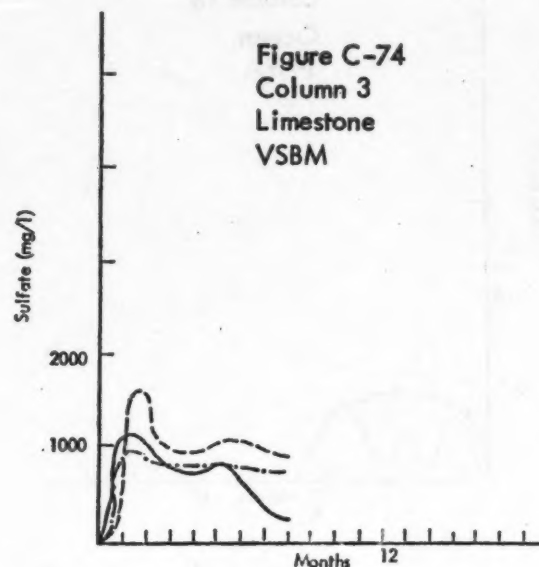
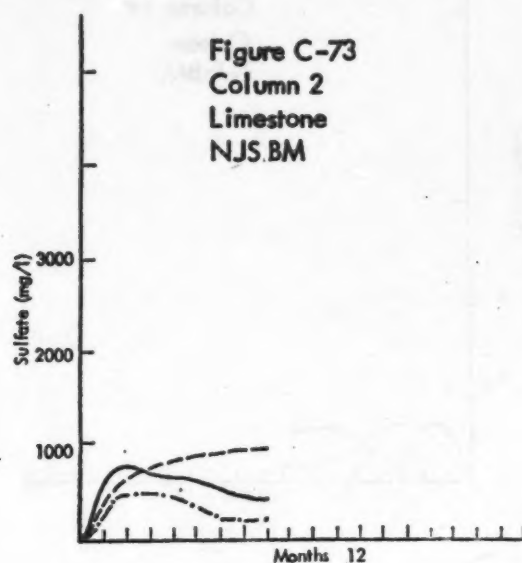
Figures C-65 - C-68. Nickel leached from Columns 14 to 17: Coal mine.



Legend.
Top lysimeter
Bottom lysimeter
Drain
Incoming water



Figures C-69 - C-72. Nickel leached from Column 18 to 20 and 1. Ocean.



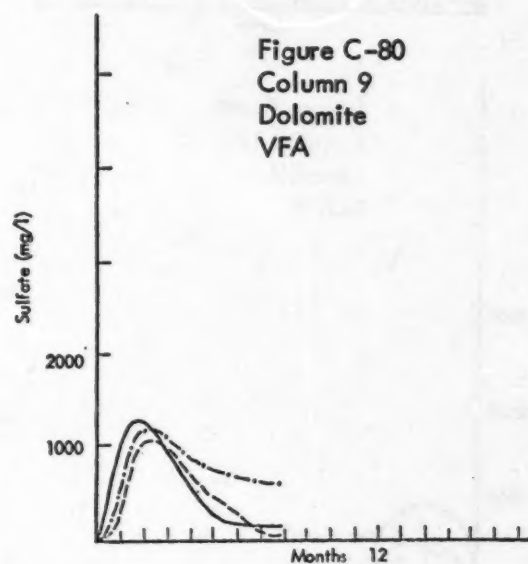
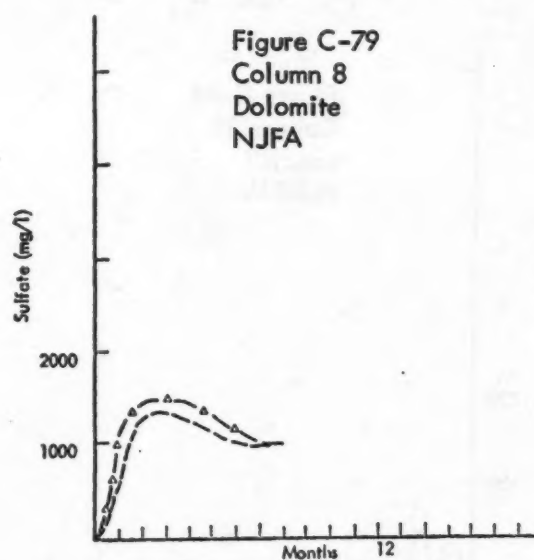
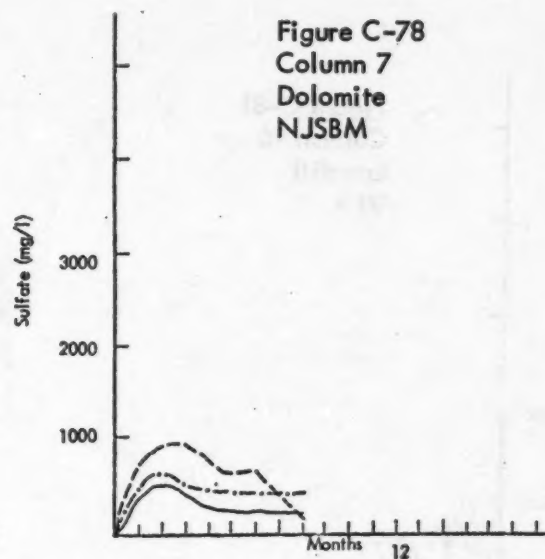
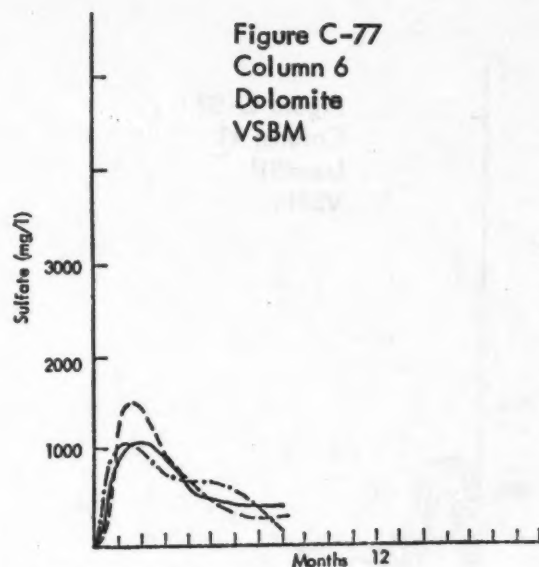
Legend

Top lysimeter - - - - -

Bottom lysimeter - . - . -

Drain —————

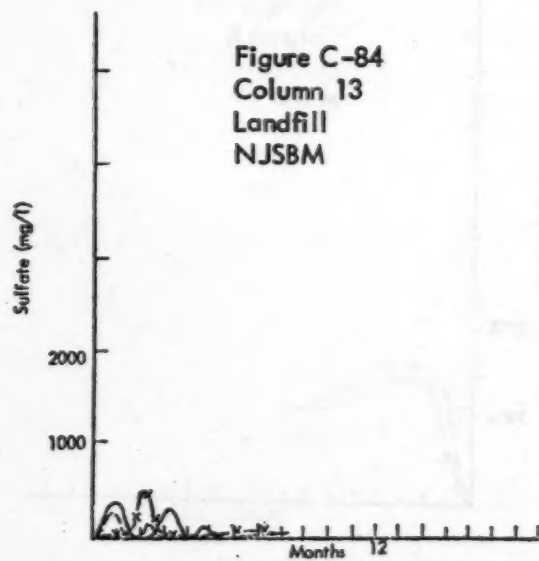
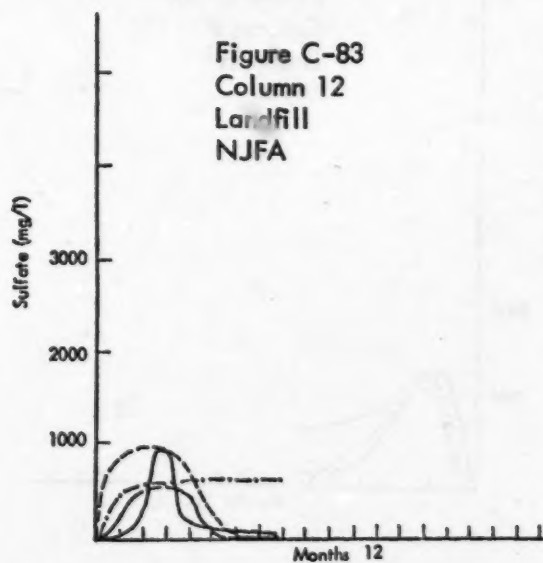
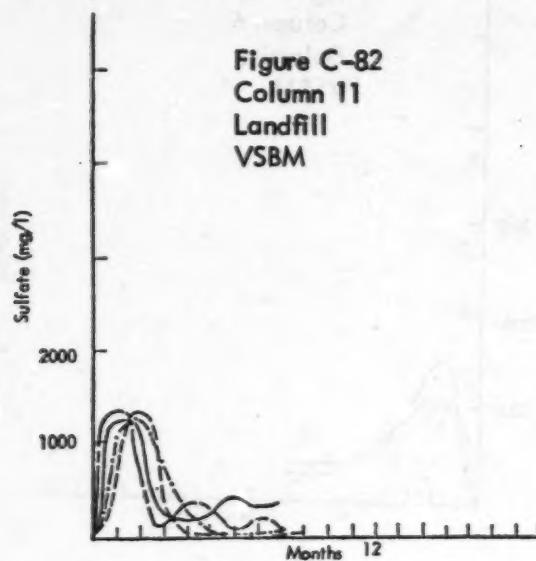
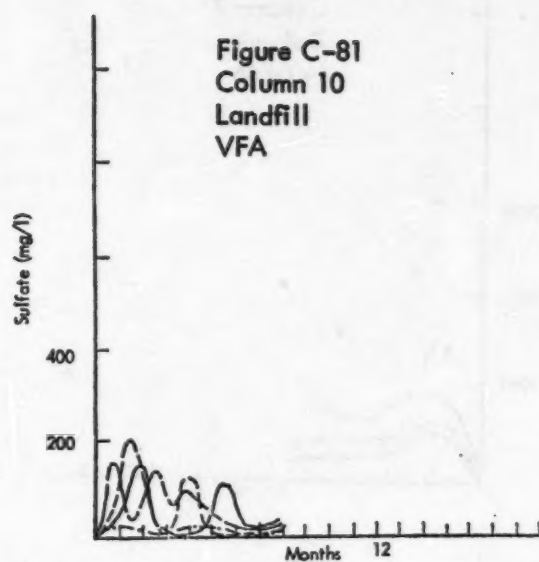
Figures C-73 - C-76. Sulfate leached from Columns 2 to 5: Limestone quarry.



Legend

Top lysimeter	-----
Bottom lysimeter	—•—•—
Drain	————
Drain and bottom lysimeter	—△—△—

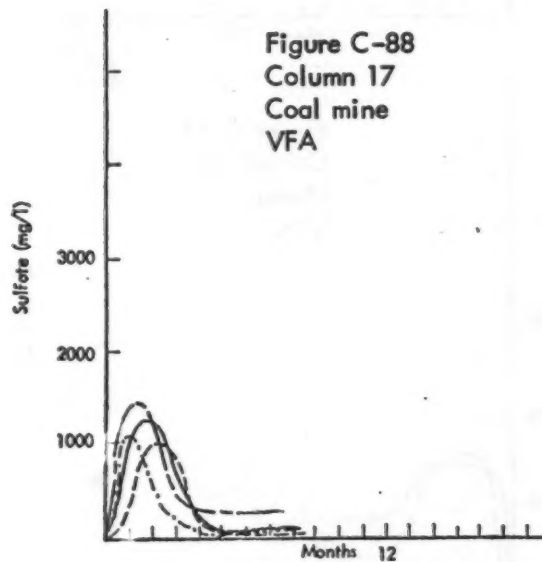
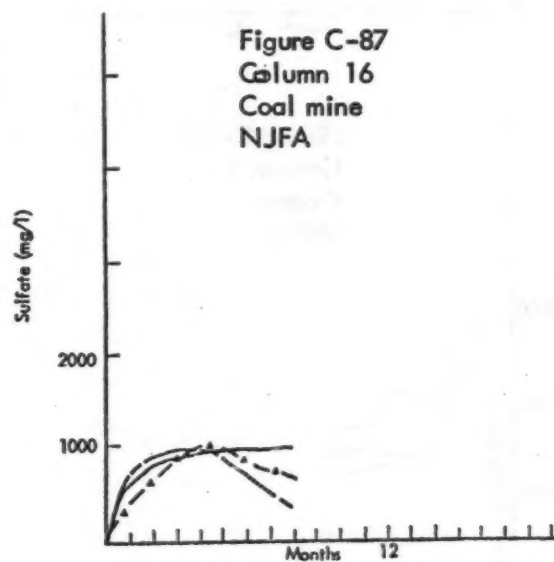
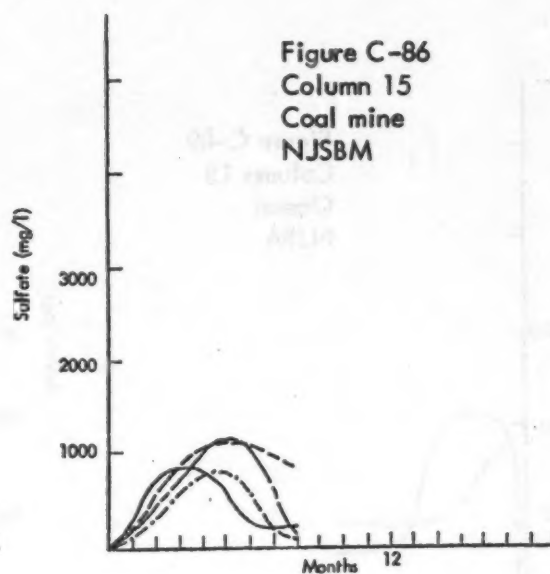
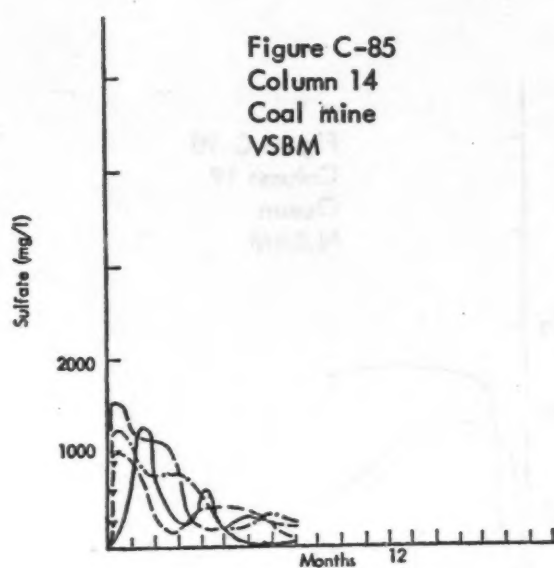
Figures C-77 - C80. Sulfate leached from Columns 6 to 9: Dolomite quarry.



Legend

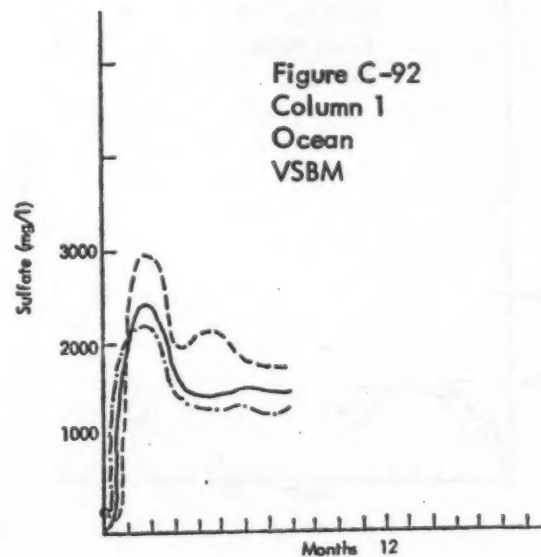
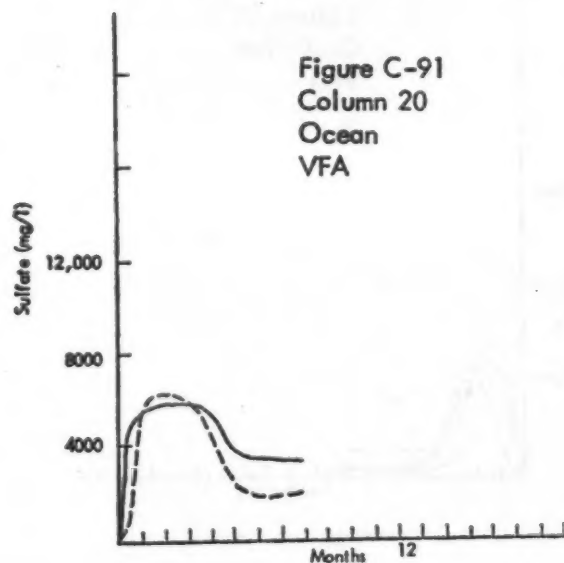
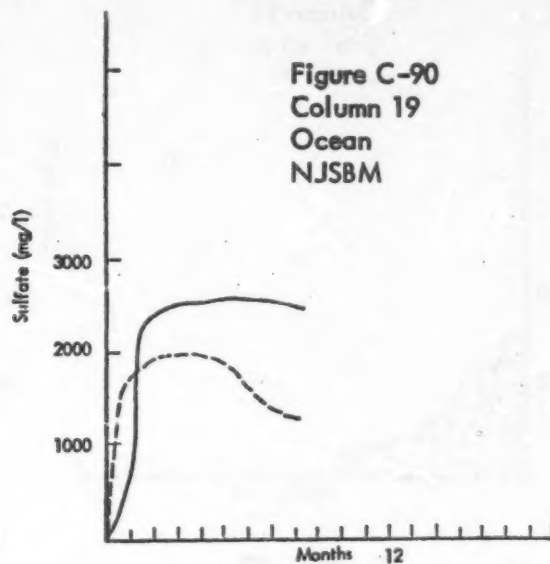
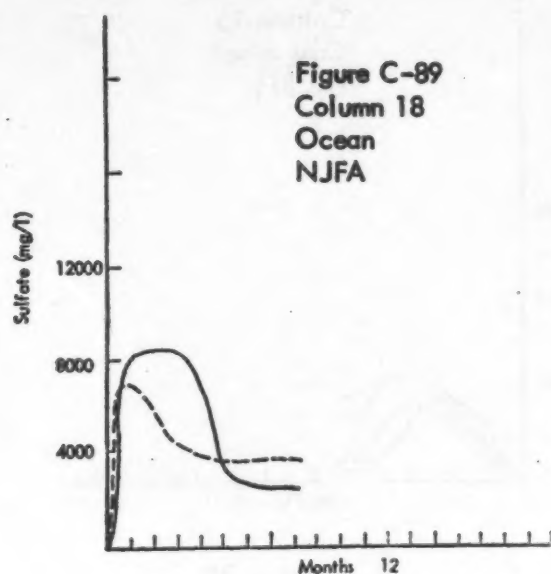
Top lysimeter	----
Middle lysimeter	-----
Bottom lysimeter	- . - . -
Drain	=====
Bottom and middle lysimeter	-X-X-

Figures C-81 to C-84. Sulfate leached from Columns 10 to 13: Sanitary landfill.



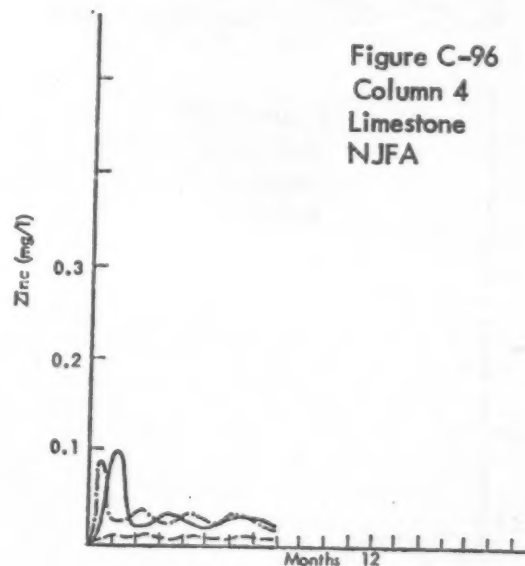
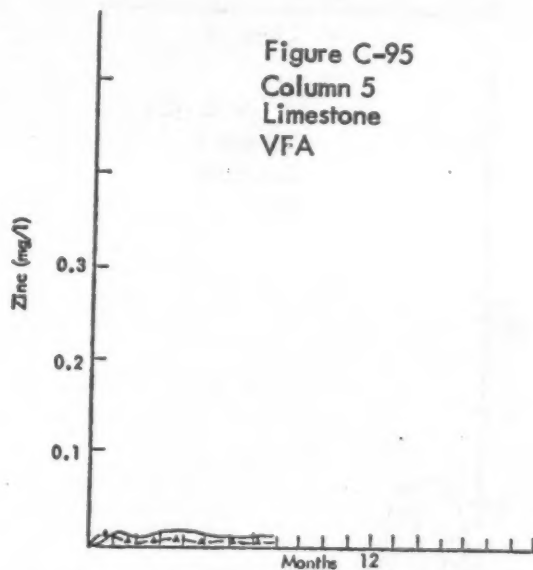
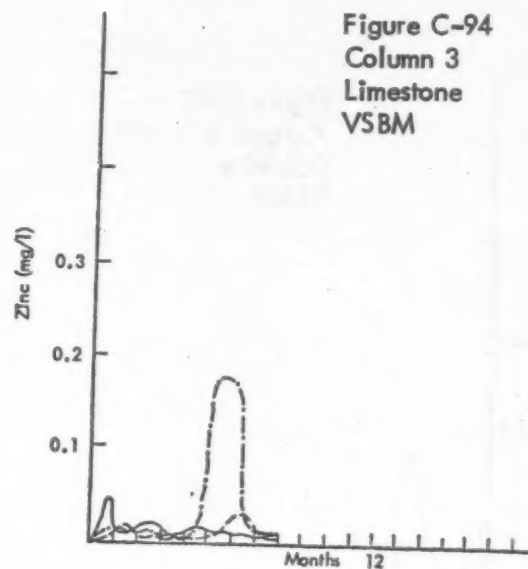
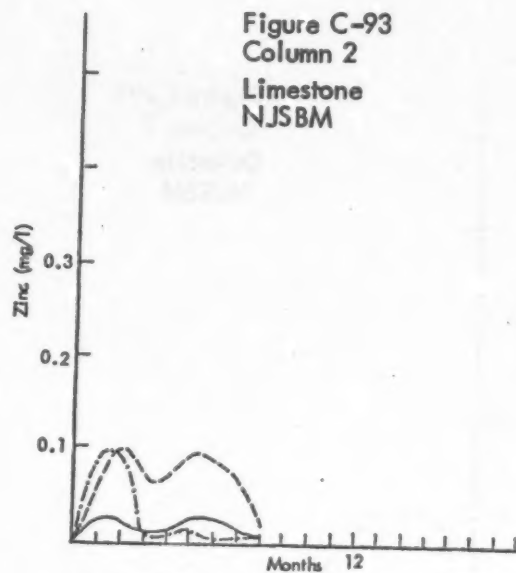
Legend			
Top lysimeter	-----	Top, middle, and bottom lysimeters	---▼---
Middle lysimeter	-----	Bottom and top lysimeters	---▲---
Bottom lysimeter	-----		
Drain	-----		

Figures C-85 - C88. Sulfate leached from Columns 14-17: Coal mine.



Legend
Top lysimeter -----
Bottom lysimeter -.-.-.-
Drain _____

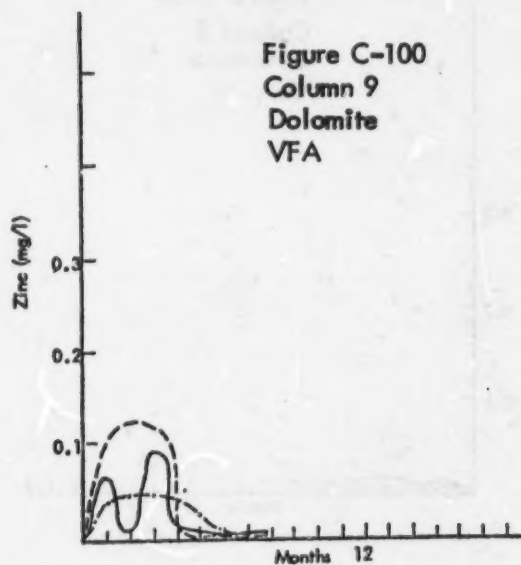
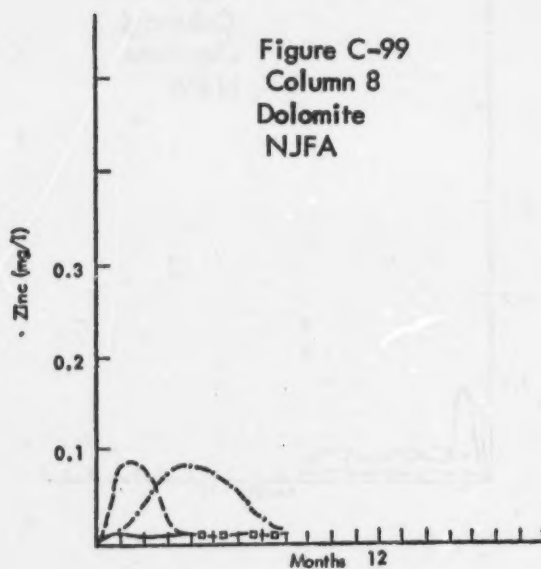
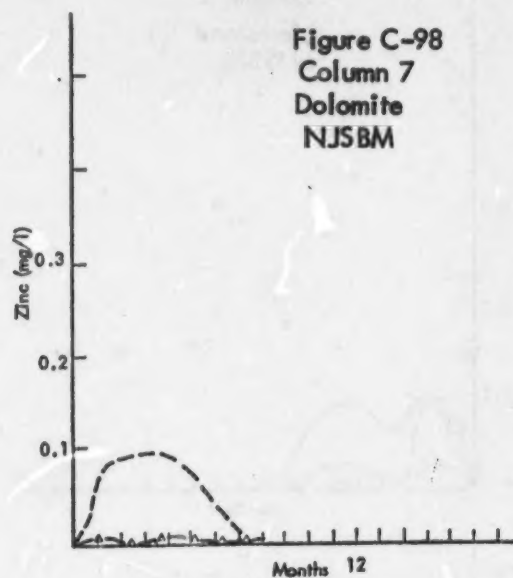
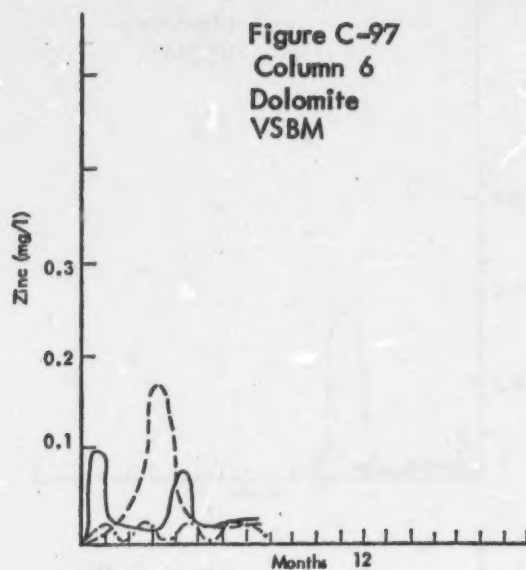
Figures C-89 - C-92. Sulfate leached from Columns 18 to 20 and 1: Ocean.



Legend

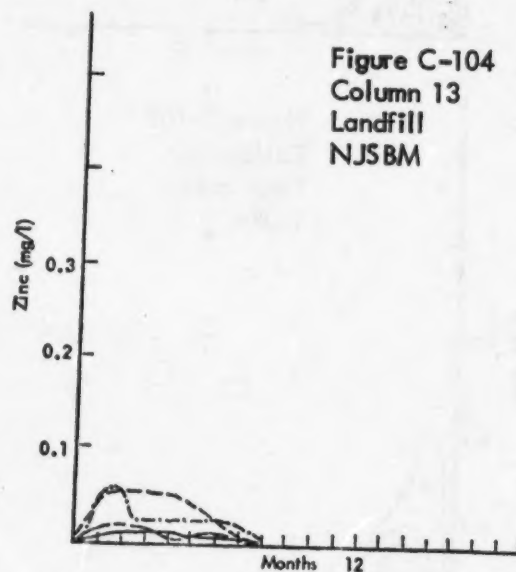
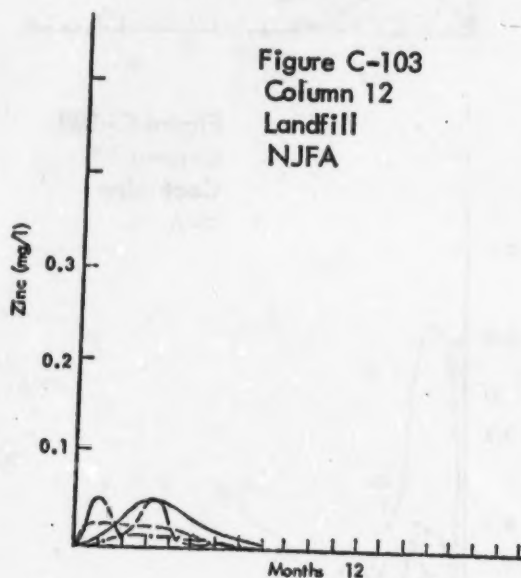
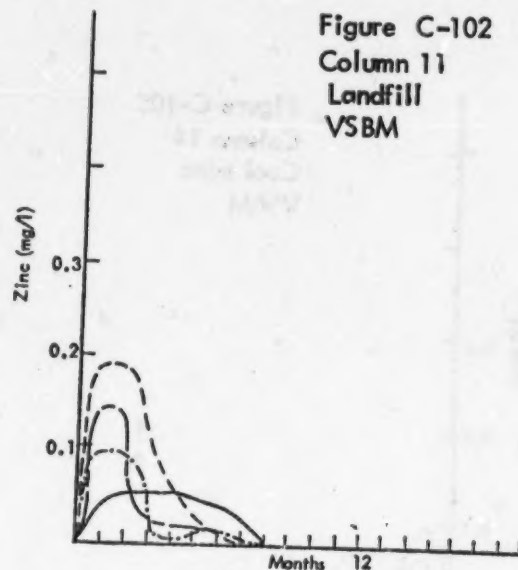
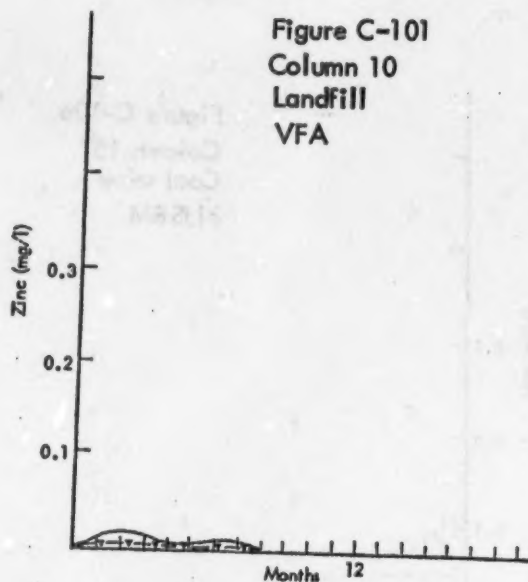
Top lysimeter	-----
Bottom lysimeter	—•—•—
Drain	————
Top and bottom lysimeters	—▲—▲—

Figures C-93 - C-96. Zinc leached from Columns 2 to 5 : Limestone quarry.



<u>Legend</u>			
Top lysimeter	-----	Drain and top lysimeter	- . - . - .
Bottom lysimeter	_____	Drain and bottom lysimeter	-----
Drain			

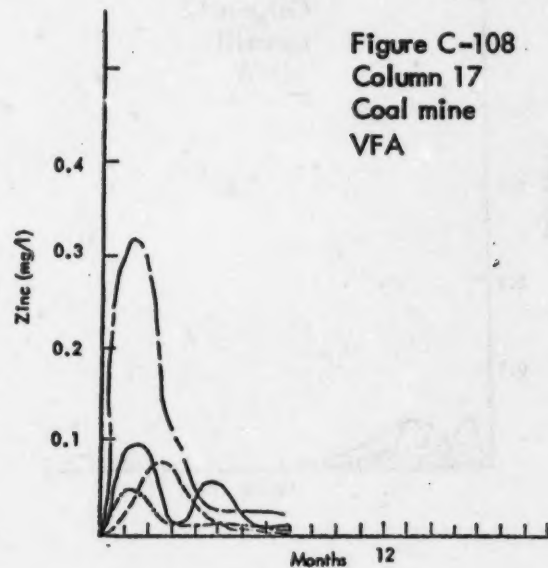
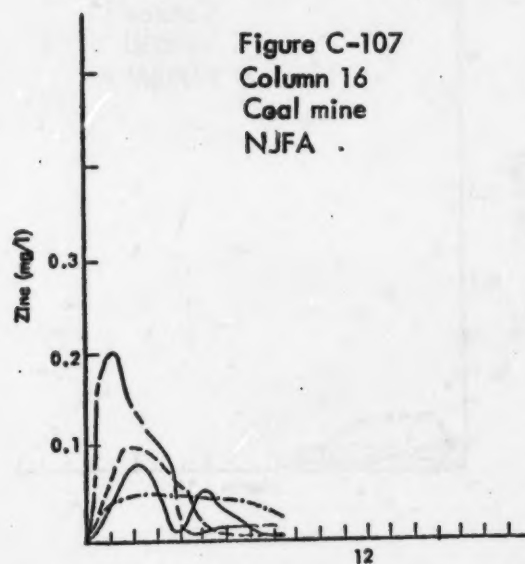
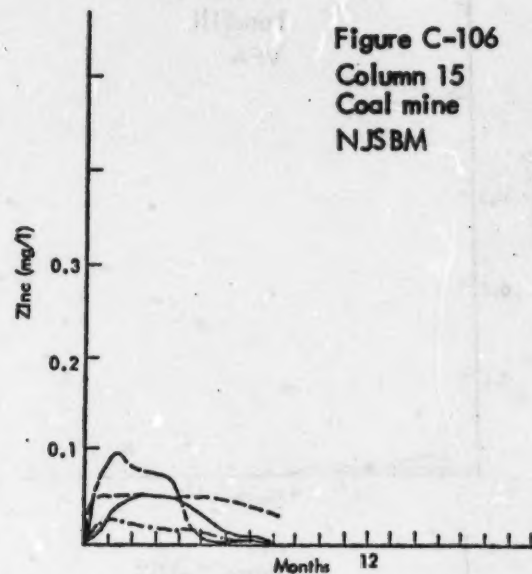
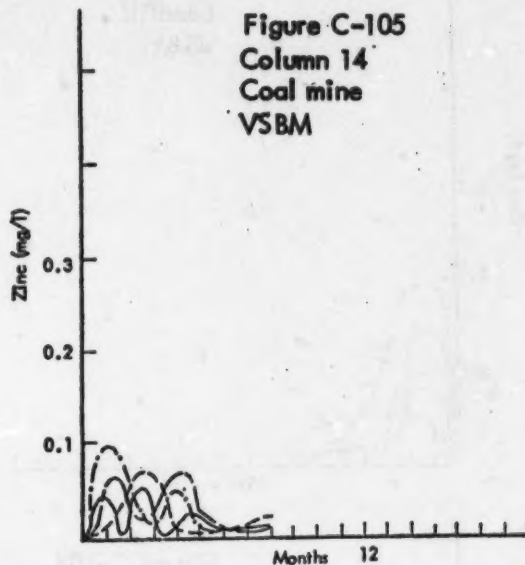
Figures C-97 - C-100. Zinc leached from Columns 6 to 9: Dolomite quarry.



Legend

Top lysimeter	-----	Bottom lysimeter	
Middle lysimeter		Top, middle, and bottom	- - - - -
Drain	=====	lysimeters	-----

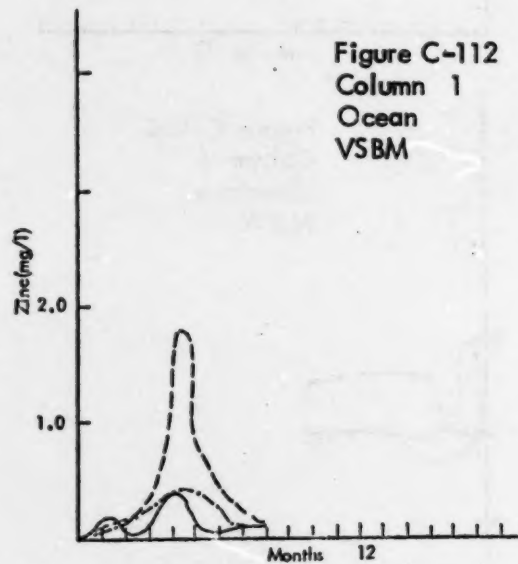
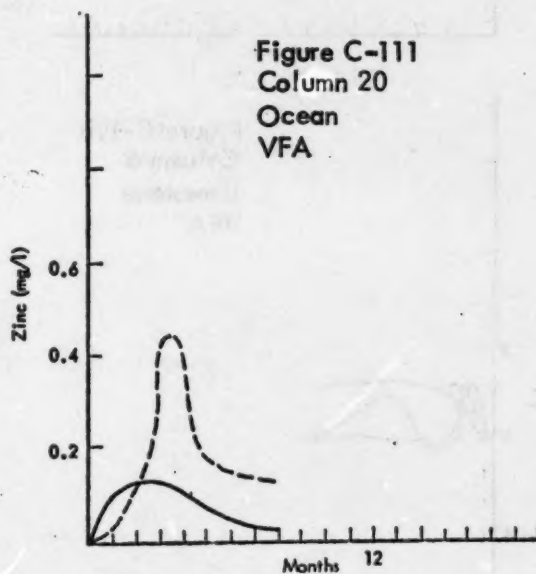
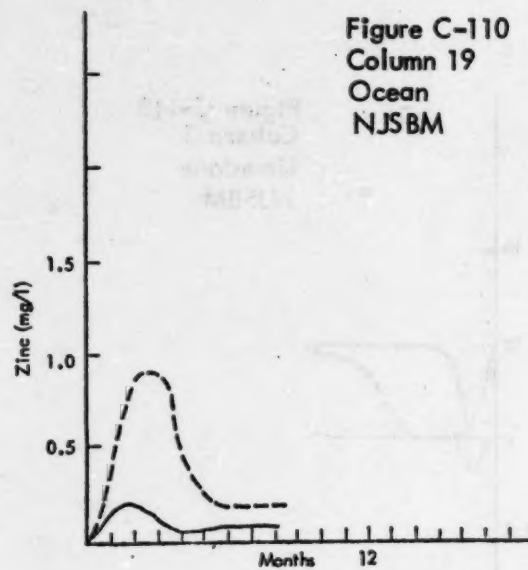
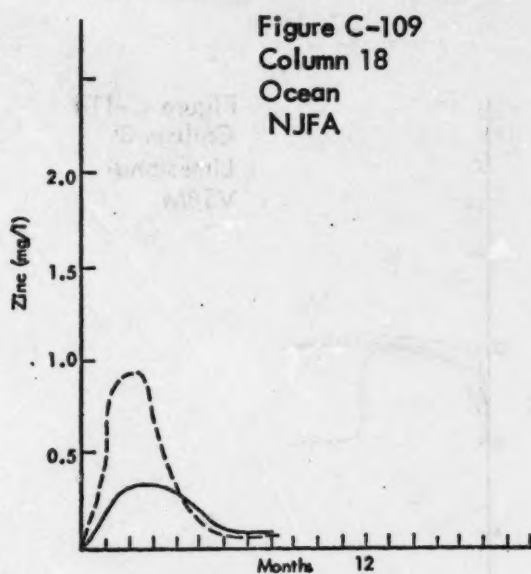
Figures C-101 - C-104. Zinc leached from Columns 10 to 13: Sanitary landfill



Legend

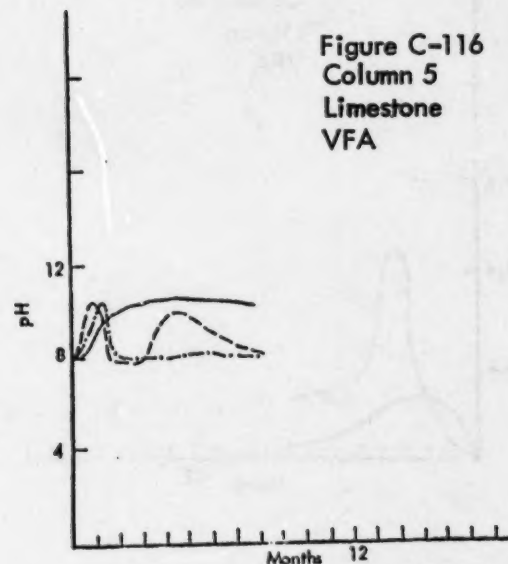
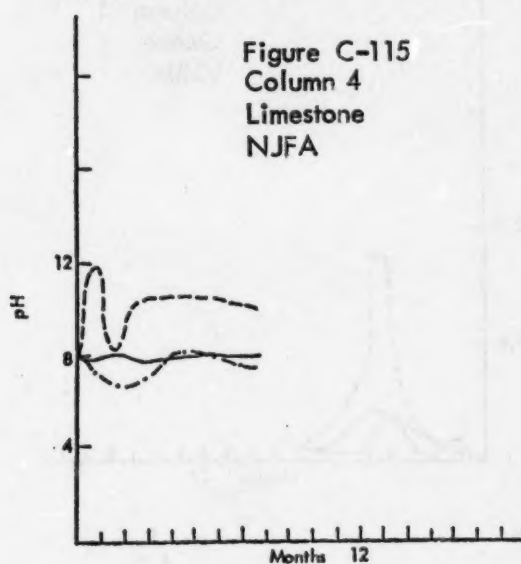
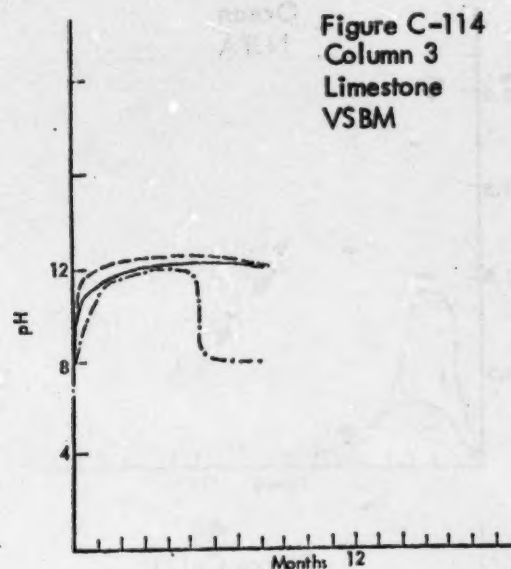
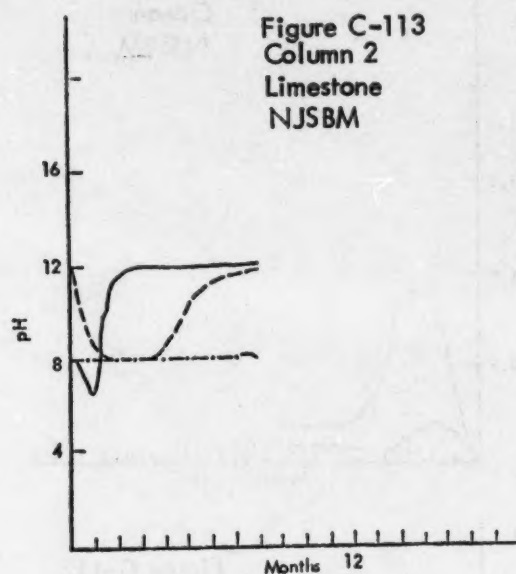
Top lysimeter	-----
Middle lysimeter	—————
Bottom lysimeter	—•—•—
Drain	—————

Figures C-105 - C-108. Zinc leached from Columns 14 to 17: Coal mine.



Legend
Top lysimeter
Drain

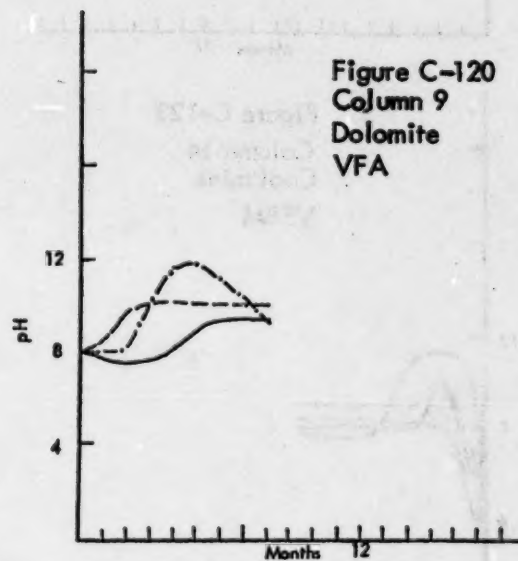
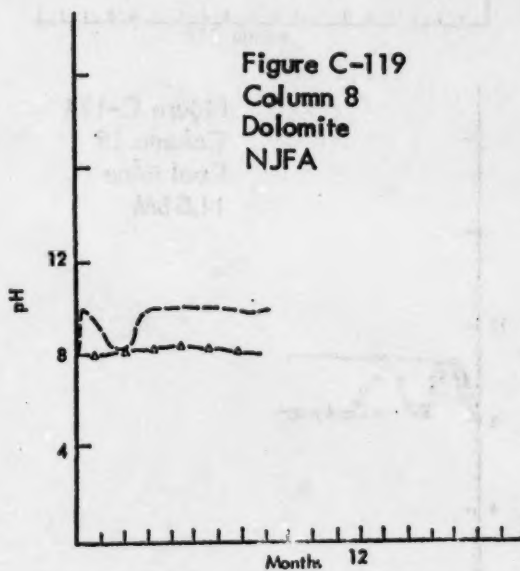
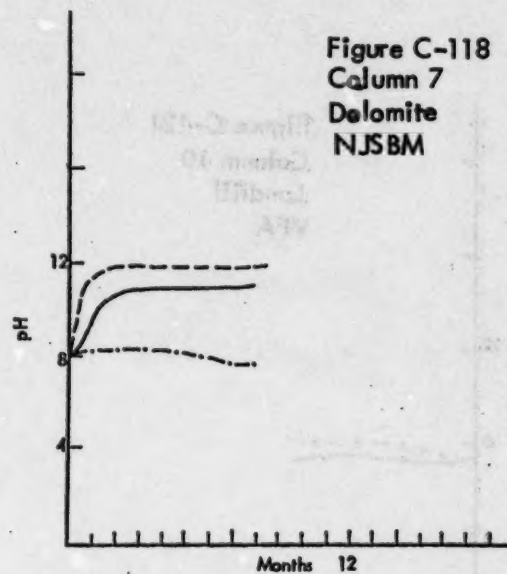
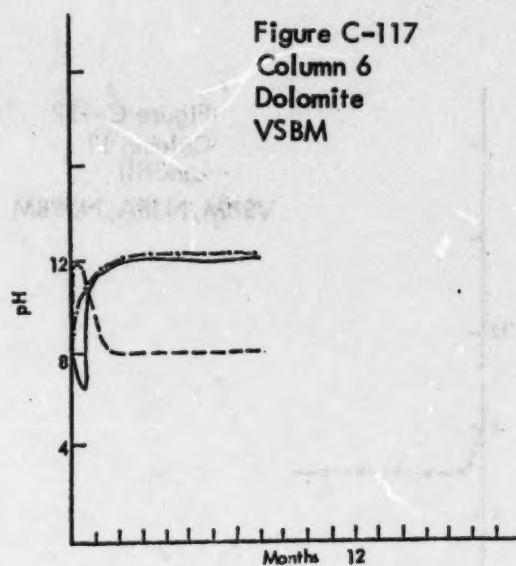
Figures C-109 - C112. Zinc leached from Columns 18 to 20 and 1: Ocean.



Legend

Top lysimeter	-----
Bottom lysimeter	—————
Drain	

Figures C-113 - C-116. pH of leachate from Columns 2 to 5: Limestone quarry.



Legend

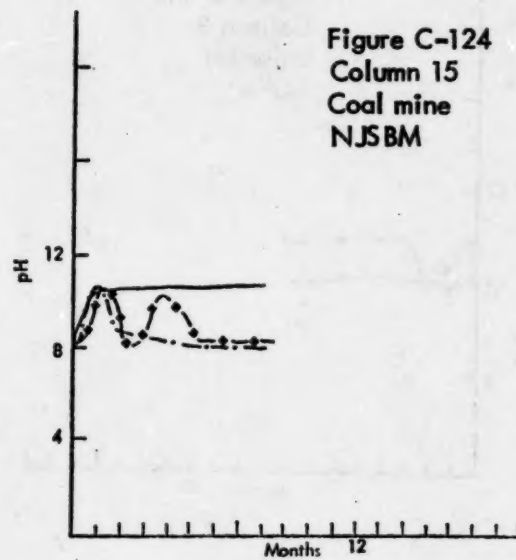
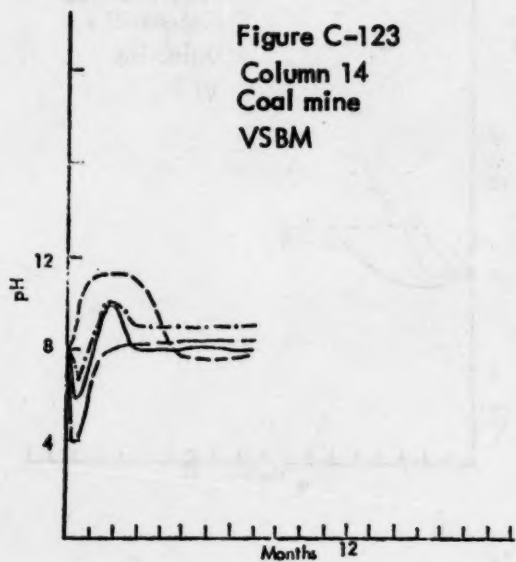
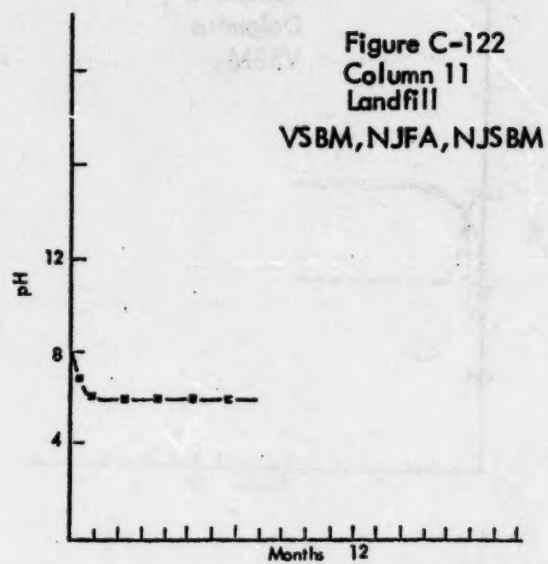
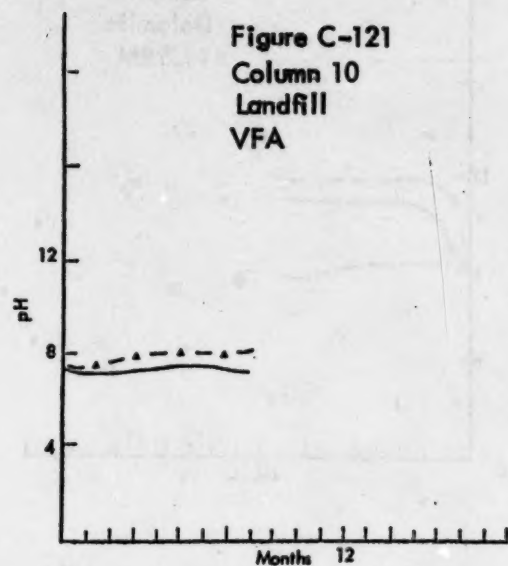
Top lysimeter ————

Bottom lysimeter ————•———

Drain ————

Drain and bottom lysimeter ————Δ———

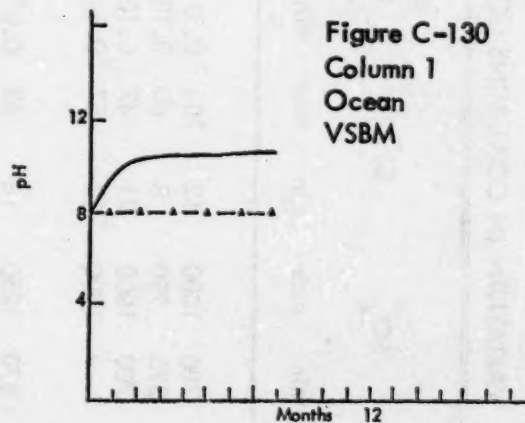
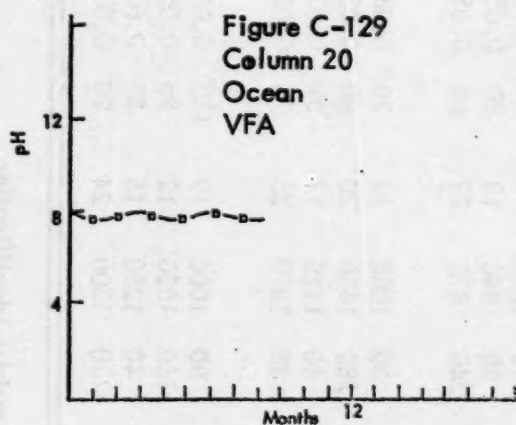
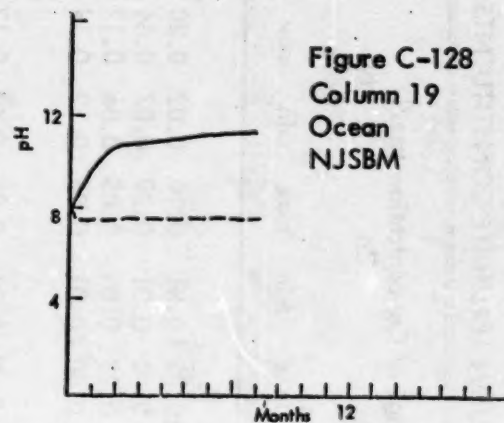
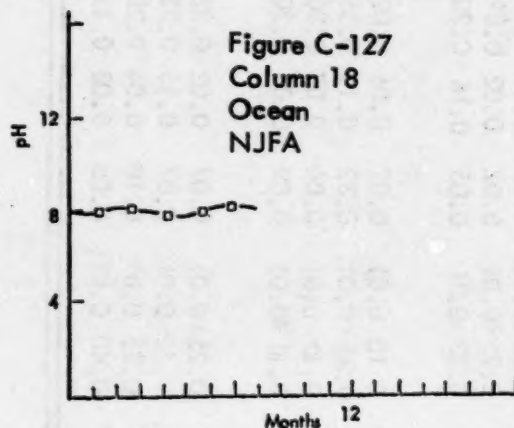
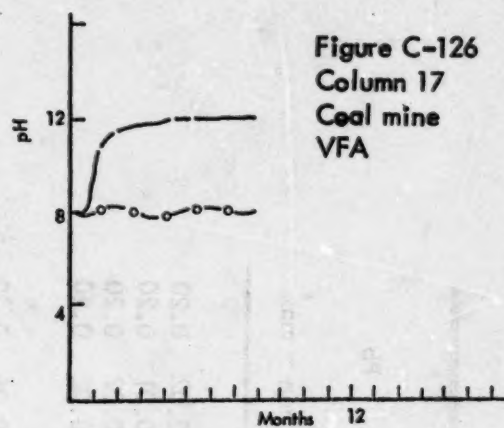
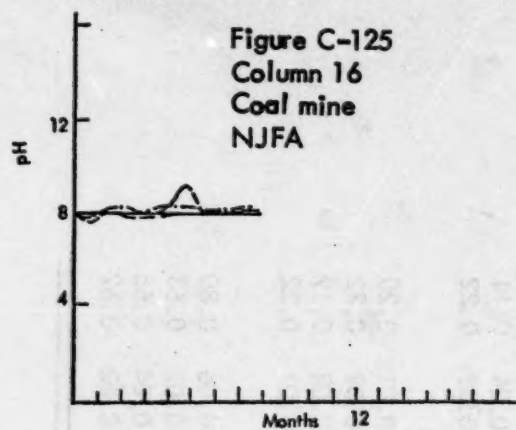
Figures C-117 - C-120. pH of leachate from Columns 6 to 9: Dolomite quarry.



Legend

Top lysimeter	-----○-----	Top and middle lysimeters	-----●-----
Middle lysimeter	-----△-----	Top, middle, and bottom lysimeter	-----▲-----
Bottom lysimeter	-----○-----	Drain and top, middle, and bottom lysimeters	-----■-----
Drain	-----		

Figures C-121 - C-124. pH of leachate from Columns 10 - 15: Sanitary landfill and ocean.



Legend

Top lysimeter	-----	Drain and top lysimeter	—○—○—
Middle lysimeter	-----	Drain and top and bottom	—○—○—
Bottom lysimeter	-----	lysimeters	—○—○—
Drain	-----		

Figures C-125 to C-130. pH of leachate from Columns 16 to 20 and 1;
Coal mine and ocean.

TABLE C-1. VARIATION IN COAL MINE COLUMN LEACHATE CONSTITUENTS

Residue ^a Type	SO ₄ ⁼		Cl ⁻		Range of Concentration (mg/l)						Pb	
					Fe		Zn		Ni			
	min	max	min	max	min	max	min	max	min	max	min	max
NJFA												
Top lysimeter	700	1000	12	103	0.10	0.23 < 0.01	0.10	0.02	0.20	0.02	0.02	0.20
Middle lysimeter	375	990	8	60	0.10	0.40	0.01	0.20	0.07	0.34	0.01	0.20
Bottom lysimeter	700	1000	21	47	0.10	0.23	0.03	0.05	0.06	0.17	0.02	0.20
Drain	--	1000	12	57	0.10	0.40 < 0.01	0.08	0.12	0.14	0.02	0.02	0.20
NJSBM												
Top lysimeter	870	1250	18	63	0.05	0.23 < 0.01	0.05	0.01	0.17	0.06	0.20	0.20
Middle lysimeter	140	1280	15	70	0.05	0.30 < 0.01	0.09	0.01	0.12	0.02	0.38	0.38
Bottom lysimeter	90	840	18	80	0.05	0.25 < 0.01	0.02	0.02	0.39	0.04	0.11	0.11
Drain	240	875	23	60	0.05	0.23 < 0.01	0.05	0.16	0.20	0.02	0.22	0.22
VFA												
Top lysimeter	30	1000	13	80	0.03	0.10	0.01	0.07	0.06	0.09	0.01	0.20
Middle lysimeter	280	1480	20	80	0.03	0.25 < 0.01	0.32	0.10	0.35	0.02	0.22	0.22
Bottom lysimeter	40	1125	17	39	0.03	0.10 < 0.01	0.06	0.07	0.30	0.02	0.19	0.19
Drain	30	1010	25	76	0.03	0.10 < 0.01	0.09	0.03	0.20	0.01	0.22	0.22
VSBM												
Top lysimeter	80	1000	19	110	0.05	0.25	0.01	0.07	0.02	0.22	0.06	0.80
Middle lysimeter	160	1550	12	96	0.05	0.40	0.01	0.07	0.15	0.32	0.02	0.63
Bottom lysimeter	40	1250	15	83	0.05	0.25	0.01	0.10	0.04	0.20	0.04	0.65
Drain	30	1300	24	90	0.05	0.40	0.01	0.05	0.08	0.12	0.02	0.62

^a See Table 6 for residue identification.

TABLE C-2. VARIATION IN SANITARY LANDFILL COLUMN LEACHATE CONSTITUENTS

Residue ^a Type	Range of Concentration (mg/l)																							
	SO ₄ ⁼				Cl ⁻				Fe				Zn				Ni				Pb			
	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max				
NJFA																								
Top lysimeter	35	1000	21	64			ND	ND																
Middle lysimeter	15	620	22	65																				
Bottom lysimeter	—	675	15	90																				
Drain	63	960	15	40																				
NJSBM																								
Top lysimeter	5	255	10	120			ND	ND																
Middle lysimeter	10	500	17	58																				
Bottom lysimeter	10	500	10	87																				
Drain	10	370	15	80																				
VFA																								
Top lysimeter	9	207	10	105			ND	ND																
Middle lysimeter	12	165	9	56																				
Bottom lysimeter	15	160	12	75																				
Drain	4	25	17	73																				
VSBM																								
Top lysimeter	140	1365	30	120			ND	ND																
Middle lysimeter	75	1370	32	117																				
Bottom lysimeter	124	1250	30	110																				
Drain	170	1260	26	115																				

^a See Table 6 for residue identification.

TABLE C-3. VARIATION IN DOLOMITE QUARRY COLUMN LEACHATE CONSTITUENTS

Residue ^a Type	SO ₄ ⁼		Cl ⁻		Range of Concentration (mg/l)						Ni		Pb	
	min	max	min	max	min	max	min	max	min	max	min	max	min	max
NJFA														
Top lysimeter	1000	1360	--	30	0.01	0.5	0.01	0.09	0.22	0.25	0.04	0.38		
Bottom lysimeter	ND	ND	ND	ND	0.01	0.5	0.01	0.09	0.06	0.14	0.05	0.17		
Drain	1000	1500	14	60	0.01	0.5	<0.01	0.01	0.02	0.30	0.03	0.16		
NJSBM														
Top lysimeter	165	950	13	107	0.01	0.3	0.02	0.1	0.08	0.27	0.05	0.80		
Bottom lysimeter	420	630	16	100	0.01	0.3	<0.01	0.02	0.05	0.25	0.02	0.20		
Drain	240	510	17	95	0.01	0.3	<0.01	0.02	0.13	0.30	0.03	0.40		
VFA														
Top lysimeter	35	1100	21	80	0.01	0.1	<0.01	0.05	0.12	0.38	0.02	0.18		
Bottom lysimeter	490	1120	35	80	0.01	0.1	<0.01	0.12	0.08	0.25	0.01	0.19		
Drain	130	1280	15	80	0.01	0.1	<0.01	0.09	0.13	0.20	0.02	0.02		
VSBM														
Top lysimeter	300	1500	15	120	0.01	0.5	0.02	0.18	0.12	0.40	0.05	0.61		
Bottom lysimeter	400	1100	12	106	0.01	0.5	<0.01	0.02	0.13	0.25	0.07	0.57		
Drain	130	1100	15	96	0.01	0.5	0.01	0.07	<0.01	0.38	0.02	0.55		

^a See Table 6 for residue identification.

TABLE C-4. VARIATION IN LIMESTONE QUARRY COLUMN LEACHATE CONSTITUENTS

Residue ^a Type	SO ₄ ⁼		Cl ⁻		Range of Concentration (mg/l)						Pb	
	min	max	min	max	min	max	min	max	min	max	min	max
NJFA												
Top lysimeter	1030	1130	5	78	0.15	0.25<0.01	0.01	0.13	0.35	0.025	0.37	
Bottom lysimeter	1030	1100	13	41	0.15	0.25 0.01	0.1	0.15	0.43	0.025	0.16	
Drain	1190	1450	14	40	0.15	0.25 0.01	0.08	0.15	0.44	0.025	0.37	
NJSBM												
Top lysimeter	—	1000	19	70	0.10	0.10 0.02	0.10	0.10	0.4	0.025	0.14	
Bottom lysimeter	200	500	--	--	0.10	1.50 0.01	0.10	0.06	0.32	0.037	0.2	
Drain	800	450	10	40	0.10	0.10<0.01	0.025	0.07	0.39	0.60	1.8	
VFA												
Top lysimeter	500	1125	15	105	0.15	0.25<0.01	0.012	0.10	0.4	0.02	0.2	
Bottom lysimeter	700	1250	14	67	0.15	0.25<0.01	0.012	0.06	0.38	0.025	0.19	
Drain	875	1000	12	38	0.15	0.25<0.01	0.01	0.05	0.2	0.025	0.18	
VSBM												
Top lysimeter	980	1680	--	110	0.15	0.25 0.01	0.05	0.02	0.36	0.05	0.6	
Bottom lysimeter	750	1125	--	105	0.15	0.25 0.01	0.17	0.07	0.38	0.10	0.78	
Drain	750	1000	--	110	0.15	0.25 0.05	0.02	0.06	0.40	0.04	0.25	

^a See Table 6 for residue identification.

TABLE C-5. VARIATION IN SEA WATER COLUMN LEACHATE CONSTITUENTS

Residue ^a	Range of Concentration (mg/l)											
	SO ₄ ⁼		Cl ⁻		Fe		Zn		Ni		Pb	
	min	max	min	max	min	max	min	max	min	max	min	max
NJFA												
Top lysimeter		3800	7000	ND	ND							
Drain		2500	8500		1.0	5.5	0.05	0.90	0.26	0.38	0.40	1.60
NJSBM					--	0.5	0.06	0.60	0.06	0.33	0.70	0.78
Top lysimeter		1250	2000	ND	ND							
Drain		2450	2550		0.5	1.4	0.15	0.90	0.06	0.24	0.15	1.03
VFA					0.5	1.4	0.05	0.17	0.06	0.24	0.16	0.85
Top lysimeter		1900	6300	ND	ND							
Drain		3400	6000		0.5	1.5	0.12	0.42	0.22	0.30	0.2	0.87
VSBM					0.5	1.5	0.02	0.12	0.23	0.27	0.63	0.90
Top lysimeter		1750	3000	ND	ND							
Bottom lysimeter		1500	2300		0.5	3.4	0.15	1.80	0.62	1.37	0.55	2.25
Drain		1500	2300		0.5	3.4	0.1	0.40	0.80	1.40	0.30	2.75
					0.5	2.8	0.05	0.40	0.35	2.0	0.30	3.00

^a See Table 6 for residue identification.

APPENDIX D

CHARACTERIZATION OF SIMILAR RESIDUES

Coal Ash

Coal ash is primarily an iron-aluminum-silicate material which contains lime, magnesia, sulfur trioxide, sodium and potassium oxides, and carbon, as well as traces of heavy metals. Although the specific composition of a coal ash is mainly dictated by the geology of the coal deposit and the operating parameters of the boiler unit, many common minerals are present in U.S. coal. A breakdown of these minerals is given in Table D-1. Table D-2 tabulates a more detailed compilation of typical coal ash chemical constituents. The soluble constituents of coal ash from distilled water are summarized in Table D-3.

During combustion, the inorganic minerals in the coal are subjected to furnace temperatures between 1400°C and 1700°C . At these temperatures the minerals will react to form mullite, quartz, hematite, and calcium-sulfate. The distribution range for these mineral phases is compiled in Table D-4.

Fly ash generally occurs as fine spherical particulates ranging in diameter from 0.5μ to 100μ , and having an average diameter of 7μ . The color of fly ash will range from light tan to gray to black, depending on the iron and carbon content. The pH of fly ash will vary from 6.5 to 11.5 and will average about 11. A summary of the typical physical properties of fly ash is presented in Table D-5. Figure D-1 diagrams the concentration range of the major constituents in U.S. fly ash.

The residue recovered from the bottom of a coal-fired boiler unit occurs as either bottom ash or slag. These residues are typically composed of gray to black porous, angular particles. Depending on the type of boiler process used, some particles will have a glassy appearance.

The fly ash modified by limestone or dolomite injection into boilers will have significantly different composition from normal fly ash. The ash compositions generated by the combustion of bituminous coal and lignite coal are compared with the ashes obtained in the limestone and dolomite injection processes in Table 53.

Municipal Incinerator Residue

During incineration, furnace temperatures are between 980°C and 1100°C , with flame temperatures at approximately 1400°C . This process results in the reduction of the incinerated refuse to 25 to 35 percent of its original weight and to less than 10 percent of its volume. The resultant residue after quenching is a wet, complex mixture of metal, glass, slag, charred and burned paper, and ash. It is the ash that is important here because its chemical composition is very similar to that of fly ash from coal-burning boilers.

TABLE D-1. COMMON MINERALS IN U.S. COALS

Pyrite, marcasite - FeS_2	Quartz - SiO_2
Chalcopyrite - CuFeS_2	Siderite - FeCO_3
Arsenopyrite - $(\text{FeS}_2 \cdot \text{FeAs}_2)$	Kaolinite - $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4^{(7)}$
Stibnite - Sb_2S_3	Dolomite - $\text{CaMg}(\text{CO}_3)_2$
Gypsum - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Apatite - $\text{Ca}_5(\text{F}, \text{Cl}, \text{OH})(\text{PO}_4)_3$
Calcite - CaCO_3	Mica - $\text{KAl}_2(\text{Si}, \text{Al})_3\text{O}_{10}(\text{OH})_2$

TABLE D-2. CHEMICAL CONSTITUENTS OF COAL ASH

Constituents	Range (%)	Average (%)
Silica (SiO_2)	20 - 60	48
Alumina (Al_2O_3)	10 - 35	26
Ferric oxide (Fe_2O_3)	5 - 35	15
Calcium oxide (CaO)	1 - 20	5
Magnesium oxide (MgO)	0.25 - 4	2
Titanium dioxide (TiO_2)	0.5 - 2.5	1
Potassium oxide ^a (K_2O)	1.0 - 4.0	2
Sodium oxide ^a (Na_2O)	0.4 - 1.5	1
Sulfur trioxide (SO_3)	0.1 - 12	2
Carbon (C)	0.1 - 20	4
Boron (B)	0.01 - 0.6	Trace
Phosphorus (P)	0.01 - 0.3	Trace
Manganese (Mn)	0.01 - 0.3	Trace
Molybdenum (Mo)	0.01 - 0.1	Trace
Zinc (Zn)	0.01 - 0.2	Trace
Copper (Cu)	0.01 - 0.1	Trace
Mercury (Hg)	0.0 - 0.02	Trace
Uranium (U)	0.0 - 0.1	Trace

^aAlkalies

Source: 88.

TABLE D-3. CHEMICAL CONSTITUENTS OF COAL ASH

Soluble Ions	Range (for 1-1.7% dry solids)
Ca^{++}	200 - 850 ppm
Mg^{++}	185 - 400 ppm
$\text{SO}_4^{=}$	200 - 250 ppm
K^{+}	Trace
Na^{+}	Trace
$\text{PO}_4^{\equiv}$	0 - 5 ppm
BO_3^{-}	0 - 10 ppm

Source: 128.

TABLE D-4. MINERAL PHASES FOUND IN COAL ASH

Phase	Percent
Quartz	0-4
Mullite	0-16
Magnetite	0-30
Hematite	1-8
Glass	50-90

Source: 126.

TABLE D-5. PHYSICAL PROPERTIES OF FLY ASH FROM PULVERIZED
COAL FIRED PLANTS

Constituents	Unit	Range
Range of particle size	microns	0.5-100
Average percent passing No. 325 sieve (44μ)	percent	60-90
Bulk density (compacted)	kg/cu m	1,100-1,300
Specific gravity		2.1-2.6
Specific area/gram	cu cm/g	3,300-6,400

Source: 69.

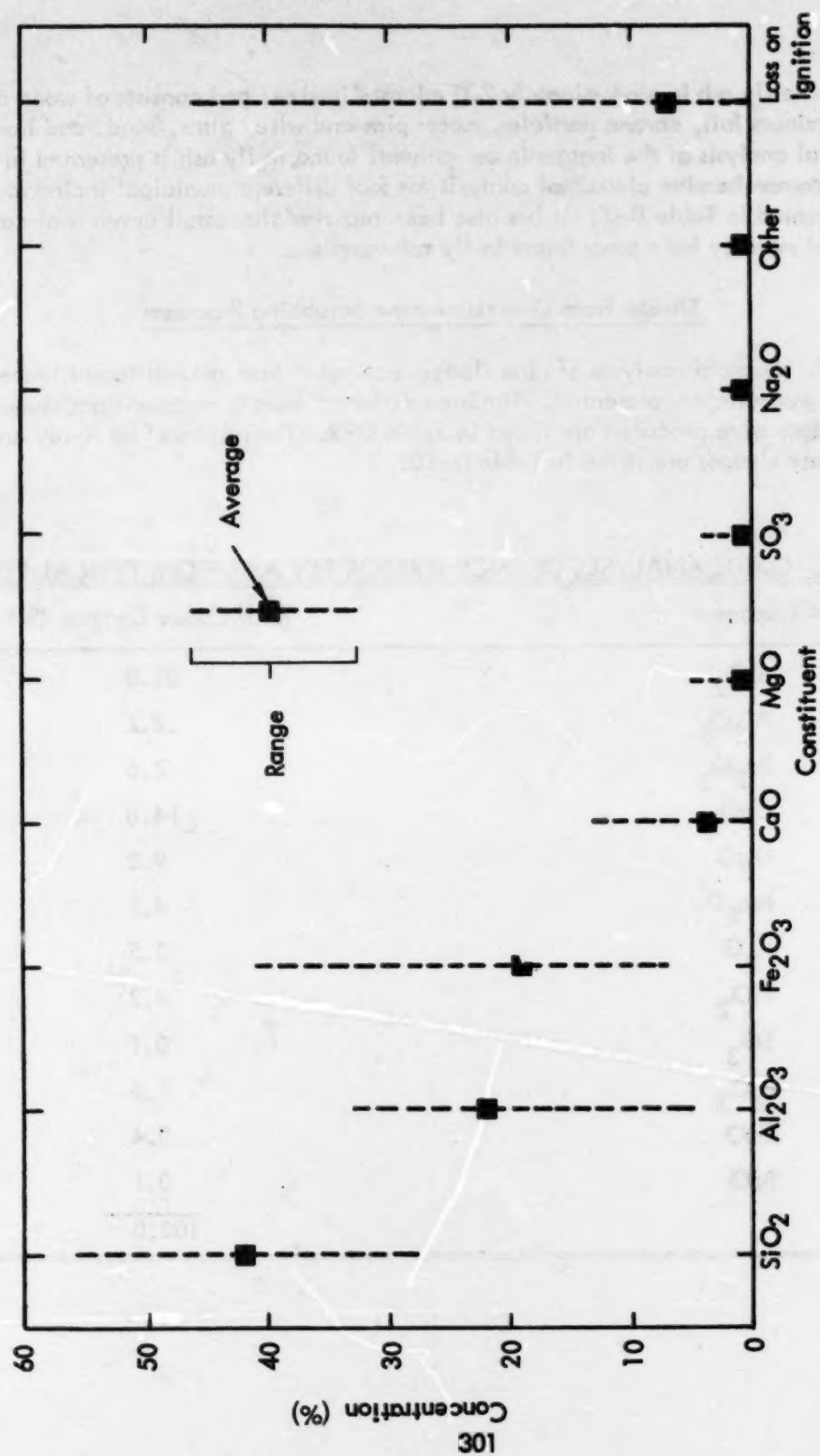


Figure D-1. Concentration range and average of U. S. fly ash constituents.

Source: 34.

In comparison, the fly ash is predominately 200 microns in size, and consists of wood and paper ash, aluminum foil, carbon particles, metal pins and wire, glass, sand, and iron scale. A general analysis of the inorganic components found in fly ash is presented in Table D-6. A comprehensive elemental analysis for four different municipal incinerator fly ashes is presented in Table D-7. It has also been reported that small amounts of cadmium, lead, and mercury have been found in fly ash samples.

Sludge From Lime-Limestone Scrubbing Processes

In Table D-8, chemical analyses of nine sludges collected from nine different lime-limestone scrubbing processes are presented. The nine different sources or conditions under which these sludges were produced are listed in Table D-9. The results of an X-ray analysis performed on these sludges are listed in Table D-10.

TABLE D-6. OXIDE ANALYSES OF INCINERATOR FLY ASH FROM TYPICAL REFUSE

Component	Total Oxide Content (%)
SiO ₂	53.0
Al ₂ O ₃	8.2
Fe ₂ O ₃	2.6
CaO	14.8
MgO	9.3
Na ₂ O	4.3
K ₂ O	3.5
TiO ₂	4.2
SO ₃	0.1
P ₂ O ₅	1.5
ZnO	0.4
BaO	0.1
	<u>102.0</u>

Source: 41.

TABLE D-7. ELEMENTAL HEAD SAMPLE ANALYSES OF MUNICIPAL
INCINERATOR FLY ASHES (% by weight)

Sample	Ag	Al	Ba	C	Ca	Cu	Cr	Fe	K	Mg	Mn	Na
F-1	0.02	11.63	0.11	5.16	5.23	0.08	0.11	3.22	1.66	0.99	0.40	1.93
F-2	0.01	11.03	0.09	0.68	6.09	0.13	0.06	3.21	0.76	0.94	0.11	2.28
F-3	0.07	13.31	0.23	0.42	4.25	0.06	0.05	2.05	1.12	0.99	0.07	1.55
F-4	0.01	11.51	0.11	11.18	4.16	0.05	0.06	2.11	1.92	0.92	0.15	1.09

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Sample	Ni	P	Pb	S	Si	Sn	Ti	Zn	Au
F-1	0.04	0.76	0.50	0.47	17.98	0.18	1.54	0.74	0.01
F-2	0.03	0.63	0.40	0.40	22.88	0.14	1.13	0.60	0.01
F-3	0.03	0.60	0.26	0.51	20.57	0.13	1.88	1.50	0.01
F-4	0.02	0.63	0.38	0.32	18.03	0.18	1.41	0.63	0.01

Source: 33.

TABLE D-8. WET CHEMICAL ANALYSIS OF SLUDGE STANDARDS^a

	STD I	STD II	STD III	STD IV	STD V	STD VI	STD VII	STD VIII	STD IX	
SiO ₂	46.7	1.5	30.7	0.79	19.4	1.1	27.7	4.6	1.2	2.0
Al ₂ O ₃	23.2	0.32	6.6	0.05	6.8	0.01	14.7	2.3	0.48	0.45
Fe ₂ O ₃	13.7	0.27	8.6	0.18	5.4	0.09	8.3	1.6	0.72	0.72
CaO	4.7	49.6	22.7	42.5	27.6	52.5	24.2	40.1	42.5	46.2
MgO	0.9	0.54	1.5	0.10	3.2	0.52	0.70	0.20	0.90	0.40
Na ₂ O	0.3	0.04	0.50	0.03	0.08	0.02	0.16	0.05	0.05	0.04
K ₂ O	2.6	0.17	1.1	0.05	0.24	0.14	1.2	0.29	0.07	0.21
TiO ₂	1.5	< 0.02	0.26	< 0.02	0.32	< 0.02	0.79	0.11	< 0.02	< 0.02
P ₂ O ₅	0.3	0.05	0.11	0.06	0.08	0.13	0.19	0.08	0.06	0.07
CO ₂	2.6	29.2	5.3	3.7	7.2	36.6	15.3	13.6	11.5	24.4
SO ₂	-	11.7	5.8	38.8	2.2	6.3	3.4	5.4	24.1	13.7
SO ₃	0.8	3.5	6.5	3.3	12.3	0.5	< 0.1	24.9	8.4	4.4
CaCO ₃	5.9	65.7	12.0	8.4	16.3	80.6	34.7	30.9	26.1	55.4

^a Standards are identified in Table D-9.

Source: 144.

TABLE D-9. IDENTIFICATION OF APCS SLUDGE STANDARDS

Standard	Description
I	Fly ash from Connecticut Light and Power Company's Devon Station.
II	C-E sludge ^a --CaCO ₃ . 150% of stoichiometric. 2,000 ppm SO ₂ .
III	Kansas Power and Light sludge.
IV	C-E sludge--Ca(OH) ₂ . 38% to 50% of stoichiometric. 50 to 60% SO ₂ removal. Slurry feed 830 liters/min. Recycle 625 liters/min with 210 liters/min blowdown.
V	Union Electric sludge.
VI	C-E sludge--CaCO ₃ . 150% of stoichiometric. 45 to 55% removal. No recycle.
VIA	Standard VI plus 50% Standard I (fly ash).
VII	C-E sludge--300 to 325% of stoichiometric. 64% SO ₂ removal. 135 kg/hr fly ash. 250 kg CaCO ₃ .
VIII	C-E sludge--120 to 130% of stoichiometric Ca(OH) ₂ . 90.8% removal. 450 liters/min Ca(OH) ₂ slurry underbed. Inlet SO ₂ 860 to 840 ppm. Outlet SO ₂ 80 ppm. 65 kg/hr Ca(OH) ₂ . No fly ash addition.
IX	C-E sludge--830 liters/min H ₂ O spray. 125 kg/hr lime feed. 150 C reaction temperature.

^a Sludge from the Combustion Engineering pilot plant.

Source: 144.

TABLE D-10. X-RAY ANALYSIS OF APCS SLUDGES

Standard	Major	Minor	Trace
I	SiO ₂ 3Al ₂ O ₃ ·2SiO ₂	Fe ₂ O ₃	CaCO ₃ Fe ₃ O ₄ CaSO ₄
III	SiO ₂	Fe ₃ O ₄ CaCO ₃ 2CaSO ₃ ·H ₂ O	3Al ₂ O ₃ ·SiO ₂ Ca(OH) ₂ CaSO ₄ MgO
IV	2CaSO ₃ ·H ₂ O	--	SiO ₂
V	SiO ₂ CaCO ₃	CaSO ₄ ·2H ₂ O	Ca(OH) ₂ 2CaSO ₃ ·H ₂ O Fe ₃ O ₄ 3Al ₂ O ₃ ·2SiO ₂
VI	CaCO ₃	2CaSO ₃ ·H ₂ O	CaSO ₄ SiO ₂
VIA	CaCO ₃	SiO ₂ 2Al ₂ O ₃ ·2SiO ₂	2CaSO ₃ ·H ₂ O CaSO ₄ Fe ₂ O ₃ —
VII	2CaSO ₃ ·H ₂ O	CaCO ₃	2CaSO ₃ ·H ₂ O CaSO ₄ ·2H ₂ O SiO ₂
VIII	2CaSO ₃ ·H ₂ O	CaCO ₃	Ca(OH) ₂ SiO ₂
IX	CaCO ₃	--	2CaSO ₃ ·H ₂ O SiO ₂ CaSO ₄ ·2H ₂ O Fe ₂ O ₃ Ca(OH) ₂

Source: 144.

APPENDIX E

DESCRIPTION OF FBC UNITS PROVIDING RESIDUES

Pope, Evans, and Robbins Process (Alexandria, Virginia)

The U.S. Energy Research and Development Administration supports one pilot-scale and one full-scale fluidized bed coal combustion unit operated by Pope, Evans, and Robbins (PER). In an earlier project on the PER unit (sponsored by the National Air Pollution Control Administration), they monitored air pollution emissions from the fluidized-bed combustion of coal under different conditions to determine those most favorable for reducing SO₂ emissions. Major test variables and ranges were:

Coal type	Medium and high sulfur
Bed temperature	815-1,038°C
Bed depth	15-51 cm
Bed material	Sintered ash and limestone
Flue gas oxygen content	0.5-5.0%
Superficial gas velocity	1.8-4.3 m/sec
Sorbent type	Dolomite 1337 Limestone 1359
Sorbent state	Raw, hydrated, and precalcined
Sorbent particle size	7-325 mesh
Fly-ash recirculation	Full range (0-80%)
Method of sorbent feed	Pneumatic feed with the coal, pneumatic feed remote from the coal feed and premixed with the coal

Tests were conducted on both pilot-scale and full-scale test units. This study tested residues from the full-scale unit located at Rivesville, West Virginia, only.

Fluidized-Bed Combustor (FBC)

The FBC tests explored SO₂ capture on a bench scale prior to a major expenditure of resources in testing the full-scale unit. Flue gas analyses, sulfur balances, and bed particle size versus time analyses were compiled for these tests. Portions of the operation also tested used salt addition for sorbent SO₂ activity enhancement, and for combustion catalysis in a once-through operation. The bench scale fluidized-bed combustor (FBC) contained a rectangular bed with dimensions 30.5 by 40.6 cm. The combustor was enclosed by an air distribution grid at the bottom, and water walls around the periphery. Side and front views

are shown in Figures E-1 and E-2.

Air passed into a plenum below the grid, through the grid buttons, and into the combustion chamber to fluidize the bed material and provide combustion oxygen. The bed material generally consisted of sintered coal ash crushed and double-screened to a mesh size of <8 to >14 (or of limestone 1359 of mesh size <8 to >20). Bed temperature depended on bed depth, which governed the total transfer surface at the water walls, and was monitored using several thermocouples spaced vertically in the combustor. The coal feed rate was about 50 kg per hour for an energy input of 3.4×10^5 kcal per hour. Before discharge, combustion products passed through a heavy gauge welded seam duct, an induced draft fan, and a dust collector. The air flow rate was monitored by a Pitot tube in the entrance duct, and a gate valve in the line provided air flow control to the unit. The coal feed rate was controlled by a variable speed drive on the coal feed screw.

Full-Scale Boiler Module (FBM)

The rectangular bed of the sub-pilot scale atmospheric pressure unit had dimensions of 51 by 40.6 cm. It was contained in a rectangular enclosure in which each wall was a row of vertical boiler tubes seal-welded gas-tight. Figure E-3 shows the internal construction of the FBM. Its cross section (46 by 183 cm) was roughly 7 times the FBC cross section. Air was directed upward from a plenum at the base of the unit through a grid and into the bed area. Firing with a coal input of 363 kg per hour, the FBM produced 14 kg per sq cm (gauge) steam at the rate of 2,268 kg per hour. Coal feed was controlled by the rotation of a star feeder while sorbent material feed was controlled by a variable speed screw drive.

Ash circulation was by pneumatic transport from the dust collector through a star feeder control. Flue gas from the FBM was mixed with ambient air in the ducting above the unit to reduce its temperature before entering the air preheater. Fly ash which dropped out of the flue gas at that point was collected in the hopper. The bulk of the fly ash was retained in a multiclone collector downstream. From the collector, the flue gas flowed through a long duct to an induced-draft fan and then to the atmosphere. A balance damper was provided in this ducting to control pressure in the combustion chamber.

In the regenerator, sulfated limestone from the primary zone was circulated continuously so that the carbon-bearing fly ash was burned at 1092°C with low excess air. SO_2 was driven off in high concentrations and lime was recovered for reuse by the reaction:

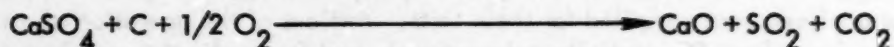
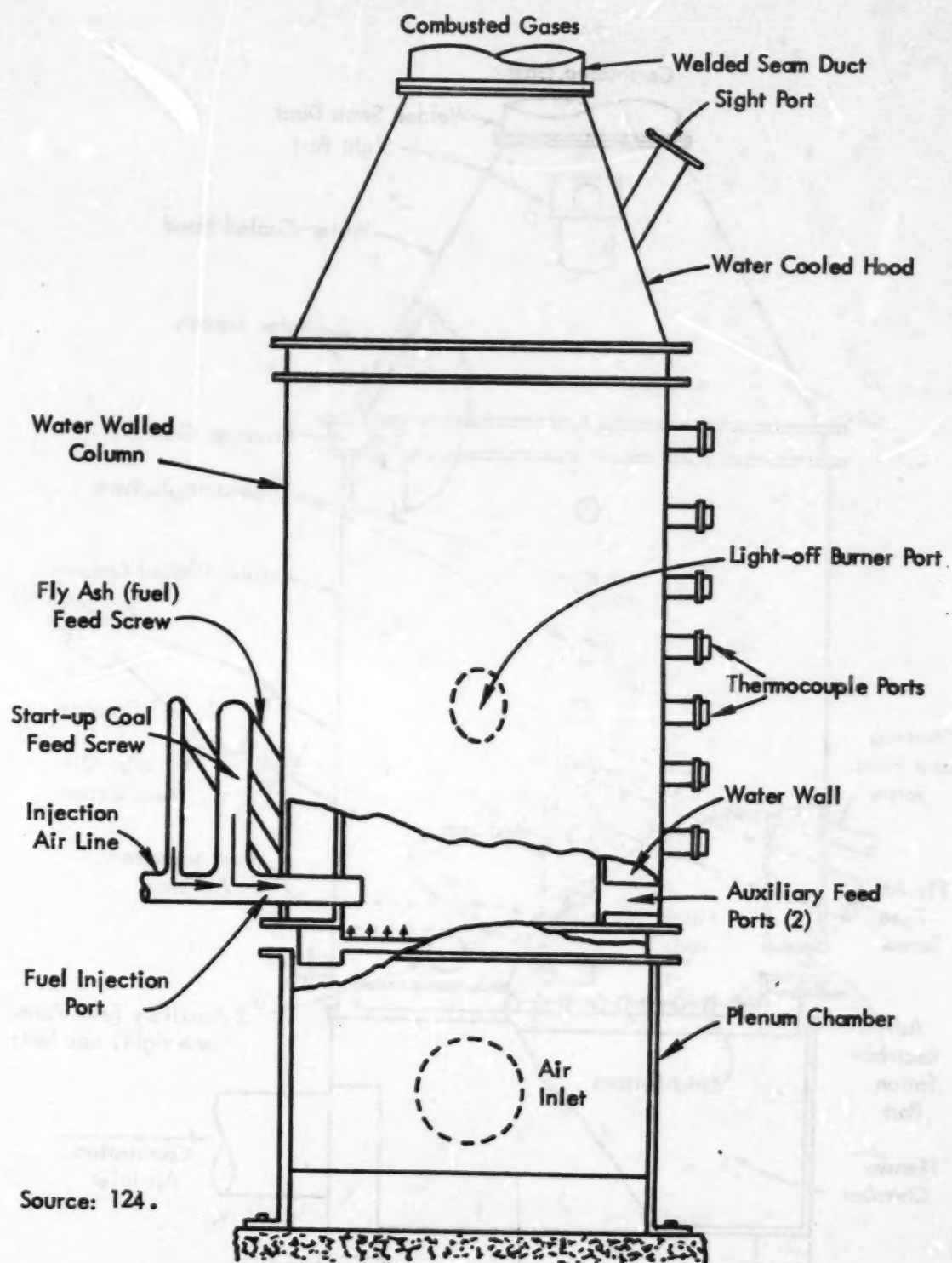
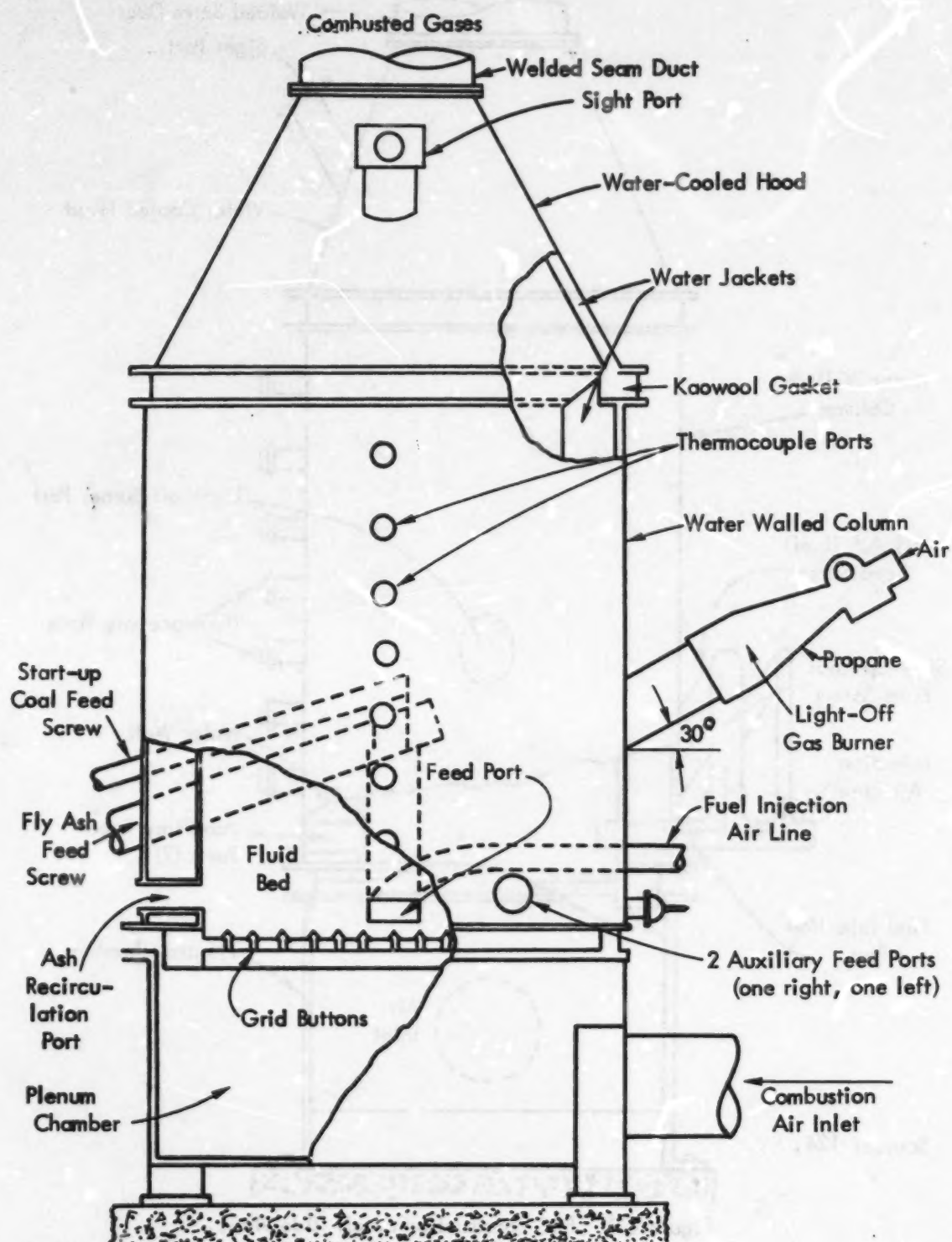


Figure E-4 is the schematic flow diagram of the FBM and regenerator. Use of fuel gas for CaSO_4 regeneration was avoided for economic reasons. Several long-duration tests were conducted with the FBM to establish the effect of different parameters on the removal of SO_2 and other pollutants.



Source: 124.

Figure E-1. FBC construction detail (side view).



Source: 124.

Figure E-2: FBC construction detail (front view) .

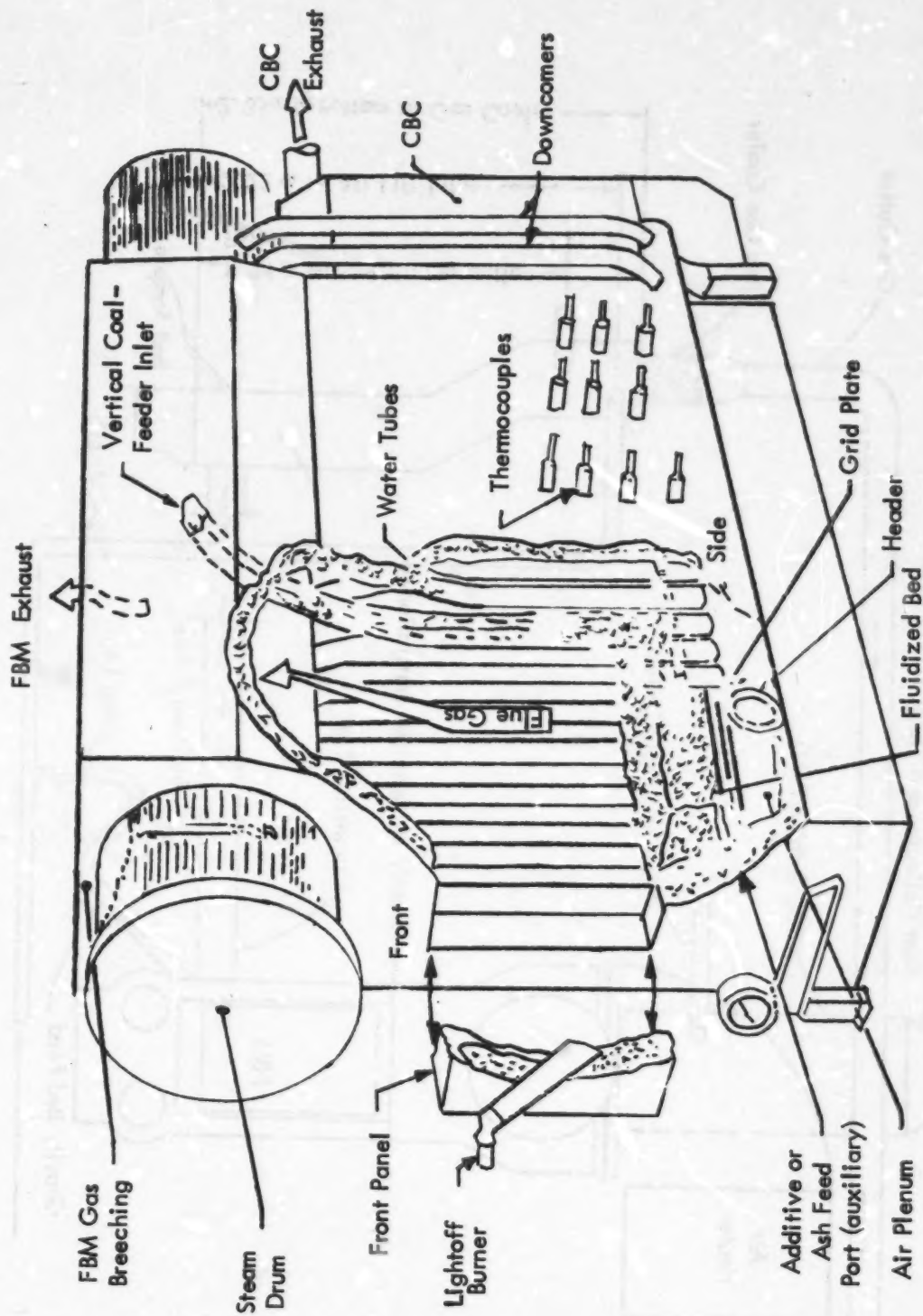


Figure E-3. Fluidized bed module: internal construction.

Source: 124.

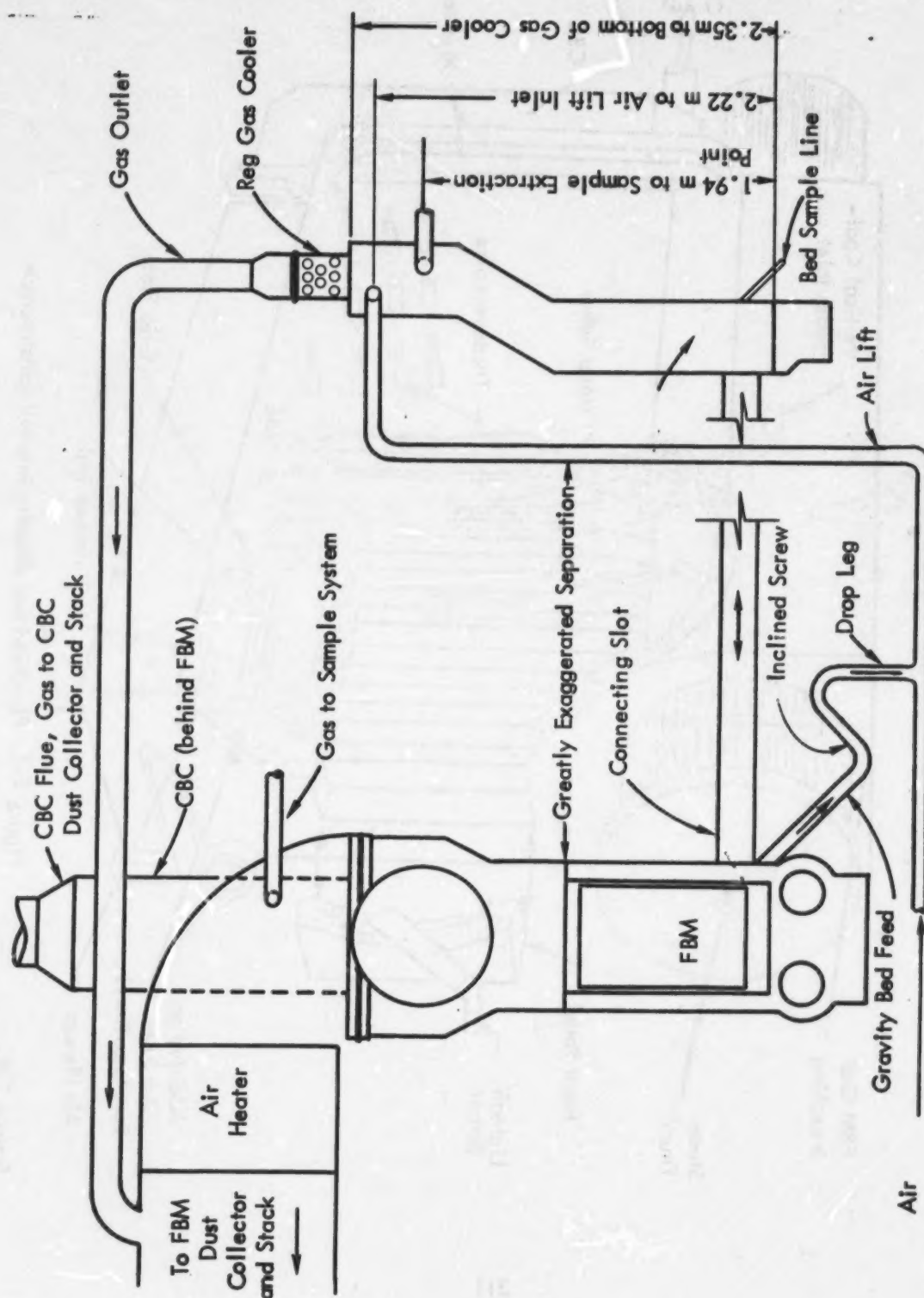


Figure E-4. FBM and regenerator flow diagram.

Source: 121.

An experimental carbon burn-up cell (CBC) was added to the FBM to raise the system carbon burn-up from 90 percent into the 98-100 percent range, and to determine the problems of operating with two distinct temperature zones (815°C in the FBM and $1,038^{\circ}\text{C}$ in the CBC). The CBC consisted of a chamber with a rectangular cross section (27 by 40 cm). The uncooled insulated walls of the CBC were fabricated of 27 percent chromium steel. The CBC was an integral part of the FBM and was located at the back of the combustor under the steam drum. Figure E-5 is the section view of the integrated FBM/CBC unit. The CBC operated continuously and burned the carbon-containing fly ash from the FBM. Coal was fed with the fly ash when ash alone could not maintain the desired $1,038\text{--}1,149^{\circ}\text{C}$ bed temperature. Fly ash from the CBC's own collector was also recycled during most tests. CBC emissions of hydrocarbons and carbon monoxide were essentially zero. Figure E-6 shows the flow path of bed material for the FBM, CBC, and regenerator.

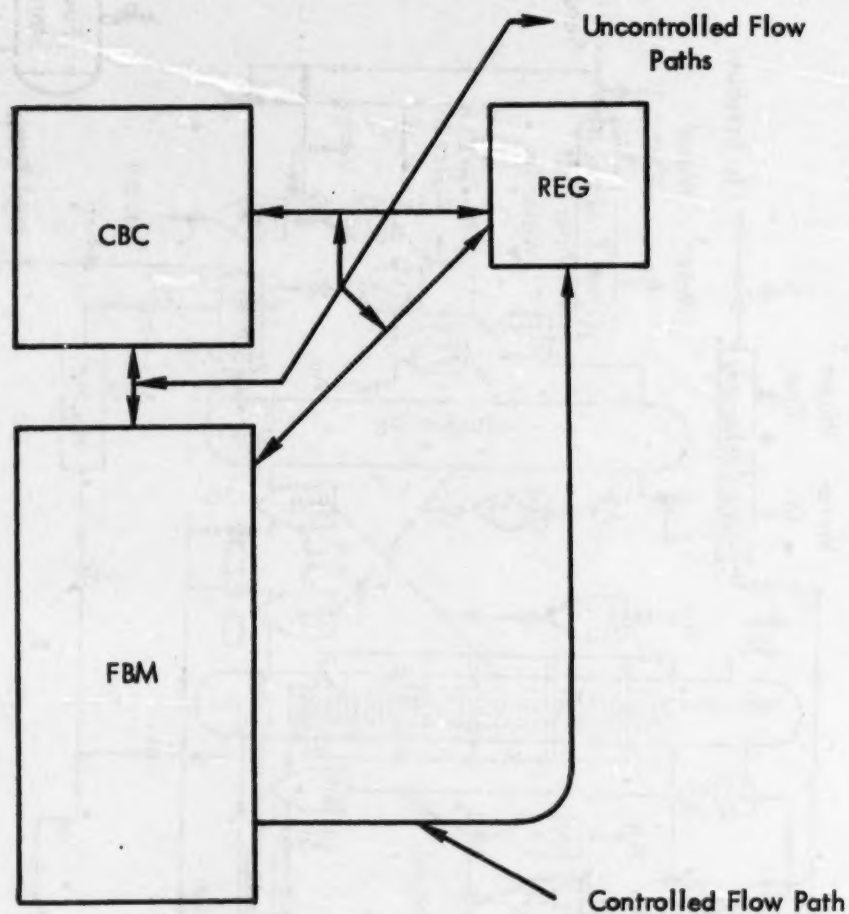
Exxon Research and Engineering's Process (Linden, New Jersey)

The U.S. EPA (Office of Research and Development) sponsored a two-phase program to investigate the feasibility of producing large amounts of heat at low SO_x emission levels by burning coal under high pressure in a fluidized bed of limestone. The first phase of the program involved the design and construction of a continuous fluidized-bed combustion/lime regeneration pilot unit--the FBCR miniplant (shown in Figure E-7). Design parameters of the process (mainly combustor and regenerator) are shown in Table E-1. The unit has been designed to operate at pressures up to 10 atmospheres with a heat release rate of about 1.5 million kcal per hour, equivalent to a power plant capacity of approximately 635 kilowatts.

The combustor was constructed from a 61-cm, refractory-lined pipe with a final inside diameter of 30 cm. It was designed with 5 flanged sections (each 0.9 m long), a bottom plenum for air intake below the removable distributor plate, and an upper bed expansion section containing the gas discharge outlet to the cyclones. The regenerator was constructed from a 46-cm pipe, refractory lined to 13 cm internal diameter.

Fluidizing air to the combustor and regenerator was supplied by a stationary compressor with a capacity of 36.8 std cu m/min. Control valves and differential pressure transmitter controlled the superficial bed velocities. In the combustor, the air passed through the distributing grid and then the fluidized bed, to a heat exchanger for cooling, and out through two refractory-lined cyclones for particulate removal. Air for the reducing-gas regenerator was electrically preheated. The reducing gas from the regenerator passed through a ceramic distributor plate supporting the regeneration bed, a refractory-lined cyclone, and a heat exchanger before being discharged through a butterfly valve. Pressure on the combustor and regenerator was kept the same by a differential pressure controlled by positioning the butterfly valve in the regenerator discharge line.

Heat extraction and temperature control in the fluidized bed was accomplished by boiling water in the vertical zones of the reactor. Solids transfer between reactors and discharge from the regenerator was accomplished using a pulsed air transport technique controlled by pressure differentials across and between the fluidized beds.



Key

↔ Bed material may flow in both directions - via gravity, pressure difference, or diffusion. Rates uncontrolled.

→ Bed material can flow only in direction of arrow with rate control.

Source: 124. Figure E-6. Bed material flow paths: FBM, CBC and regenerator.

TABLE E-1 DESIGN PARAMETERS: EXXON MINIPLANT

Parameter	Unit	Component	
		Combustor	Regenerator
Unit dimensions			
Height	cm	71.10	48.30
Internal diameter	cm	31.75	12.70
Maximum operating conditions			
Temperature	°C	927	1,093
Pressure	atm	10	10
Superficial bed velocity	m/sec	3.05	1.52
Heat released by combustion	10 ³ kcal/hr	1,588	--
Cooling load	10 ³ kcal/hr	907	--
Maximum material rates			
Air	std cu m/min	33.98	2.55
Coal	kg/hr	218	--
Limestone	kg/hr	30.84	--
Natural gas	std cu m/min	--	0.28
SO ₂ output	kg/hr	--	18.14

Source: 43.

TABLE E-1. DESIGN PARAMETERS, EXXON FLUID BED COMBUSTION UNIT

The second phase of the program involved a study of the factors influencing the formation and the control of nitrogen oxides (NO_x) in fluidized bed combustion. For these studies, a 7.6 cm ID fluidized bed combustor and two smaller electrically heated fixed bed reactors were used. An automatic instrument continuously measured NO , SO_2 , and O_2 emissions. The operating factors that were studied included excess air level, temperature, and bed composition.

The 7.6-cm unit was modified to operate as a two-stage combustor, in order to test a reactor configuration that would yield low NO_x emissions by promoting the reduction of NO by CO and then the reaction of NO with SO_2 and lime. Operating at substoichiometric conditions, the NO - CO reaction was permitted and secondary air was added at a higher point in the bed to complete the combustion and provide SO_2 for reaction with the remaining NO . A schematic diagram of the Exxon fluid bed combustion unit is shown in Figure E-8.

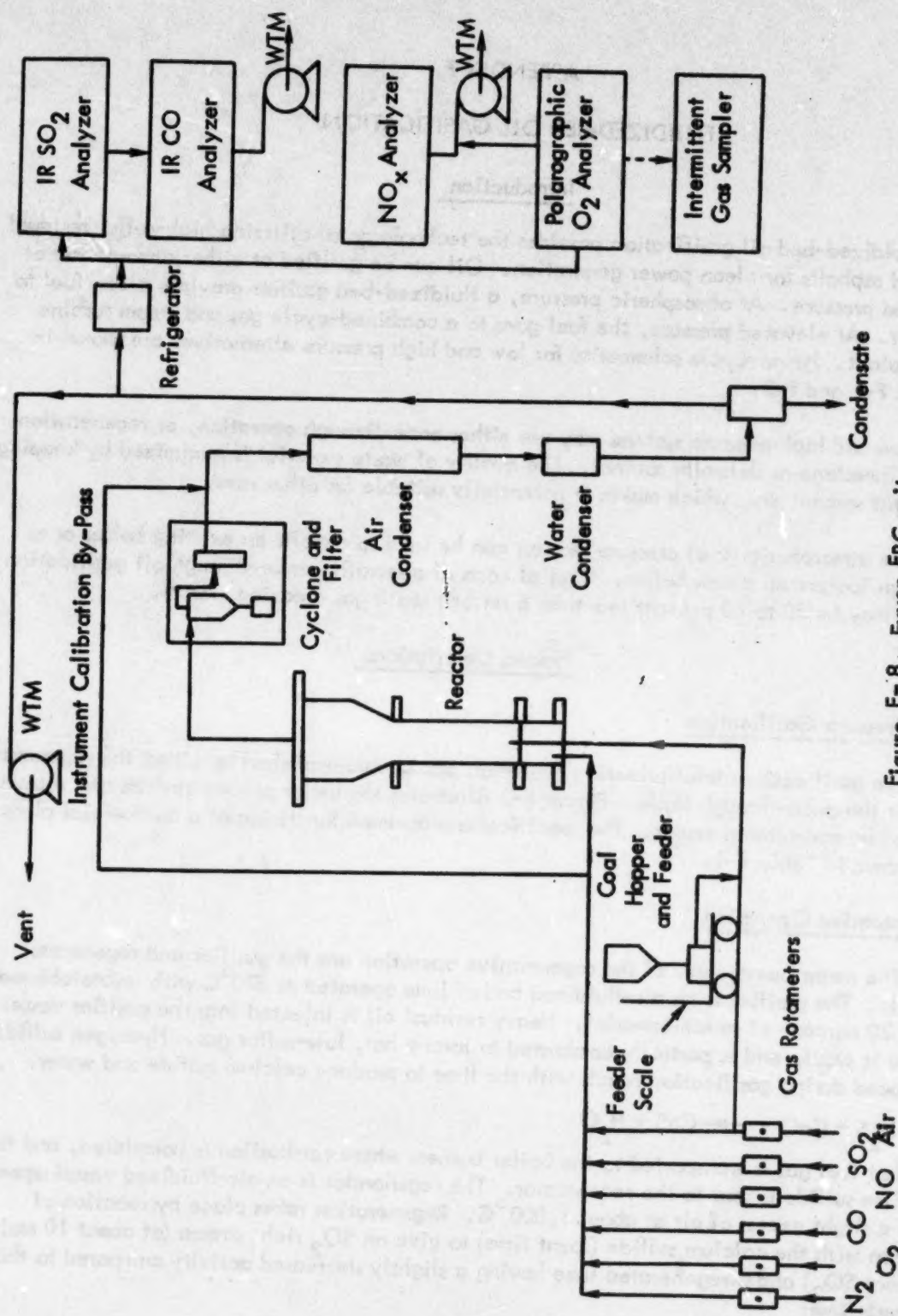


Figure E-8 • Exxon FBC unit.

Source: 43

APPENDIX F

FLUIDIZED-BED OIL GASIFICATION

Introduction

Fluidized-bed oil gasification provides the technology for utilizing high-sulfur residual oils and asphalts for clean power generation. Oil can be gasified at either atmospheric or elevated pressure. At atmospheric pressure, a fluidized-bed gasifier provides clean fuel to a boiler. At elevated pressure, the fuel goes to a combined-cycle gas and steam turbine power plant. Power-cycle schematics for low and high pressure alternatives are shown in Figures F-1 and F-2.

Low and high pressure systems may use either once-through operation, or regeneration of the limestone or dolomite sorbent. The quality of waste material is minimized by keeping the spent sorbent dry, which makes it potentially suitable for other uses.

The atmospheric (low) pressure process can be used to retrofit an existing boiler or as a design feature on a new boiler. Capital costs of a retrofit, once-through oil gasification system may be 50 to 70 percent less than a retrofit stack gas cleaning system.

Process Descriptions

Low-Pressure Gasification

The gasification/desulfurization operation can be accomplished by either the regenerative or the once-through mode. Figure F-3 illustrates the major process streams and elements of the two operational modes. The specifications assumed for design of a commercial plant are shown in Table F-1.

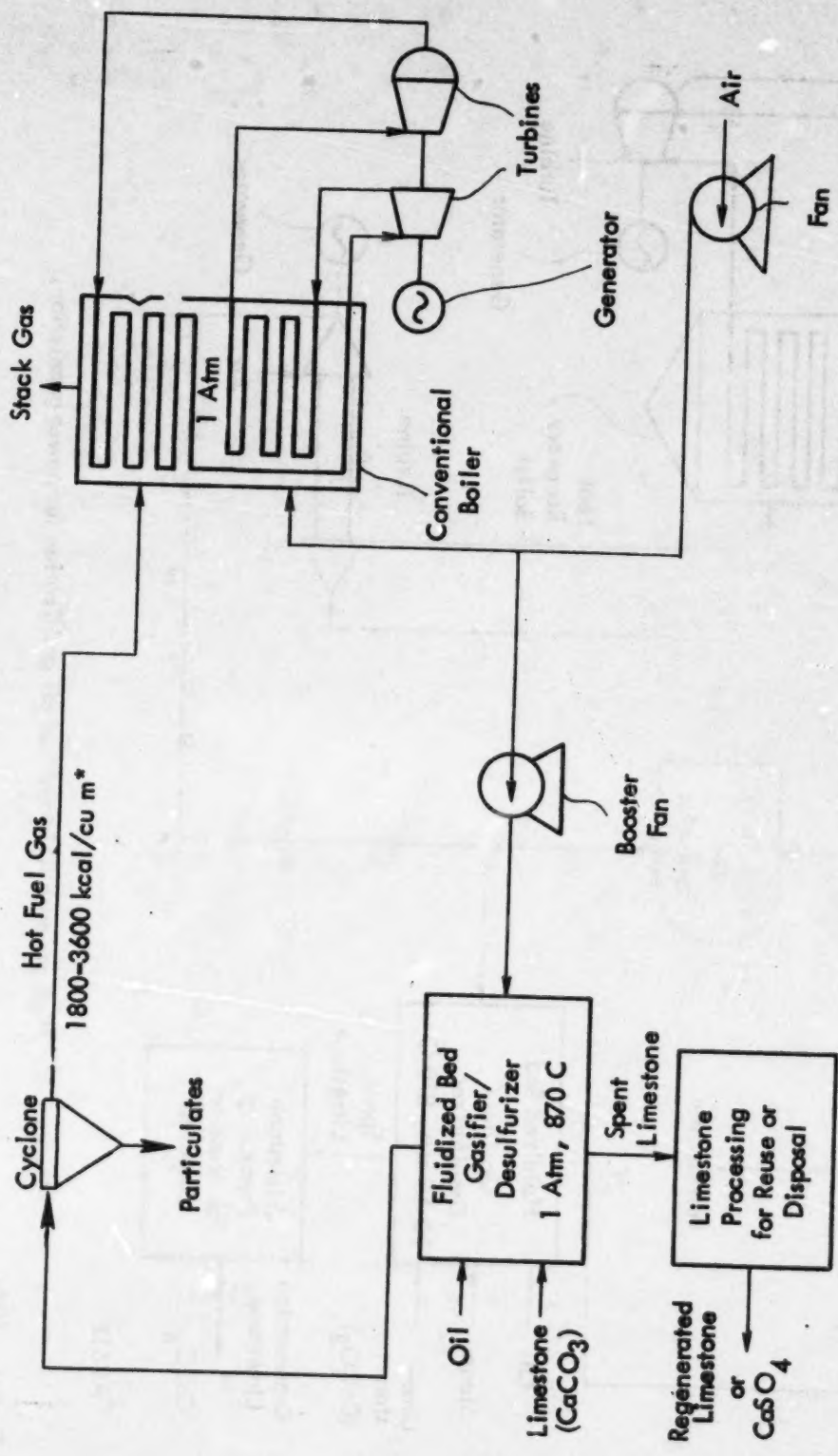
Regenerative Operation

The major components of the regenerative operation are the gasifier and regenerator vessels. The gasifier is an air-fluidized bed of lime operated at 870°C with substoichiometric air (≈20 percent of stoichiometric). Heavy residual oil is injected into the gasifier vessel where it cracks and is partially combusted to form a hot, low-sulfur gas. Hydrogen sulfide produced during gasification reacts with the lime to produce calcium sulfide and water:



The hot fuel gas is transported to the boiler burners where combustion is completed, and the calcium sulfide is sent to the regenerator. The regenerator is an air-fluidized vessel operated with a slight excess of air at about 1,000°C. Regeneration takes place by reaction of oxygen with the calcium sulfide (spent lime) to give an SO₂ rich stream (of about 10 mole percent SO₂) and a regenerated lime having a slightly decreased activity compared to that of fresh lime:





* At STP.
Source: 104.

Figure F-1. Low pressure fluidized bed oil gasification for power generation.

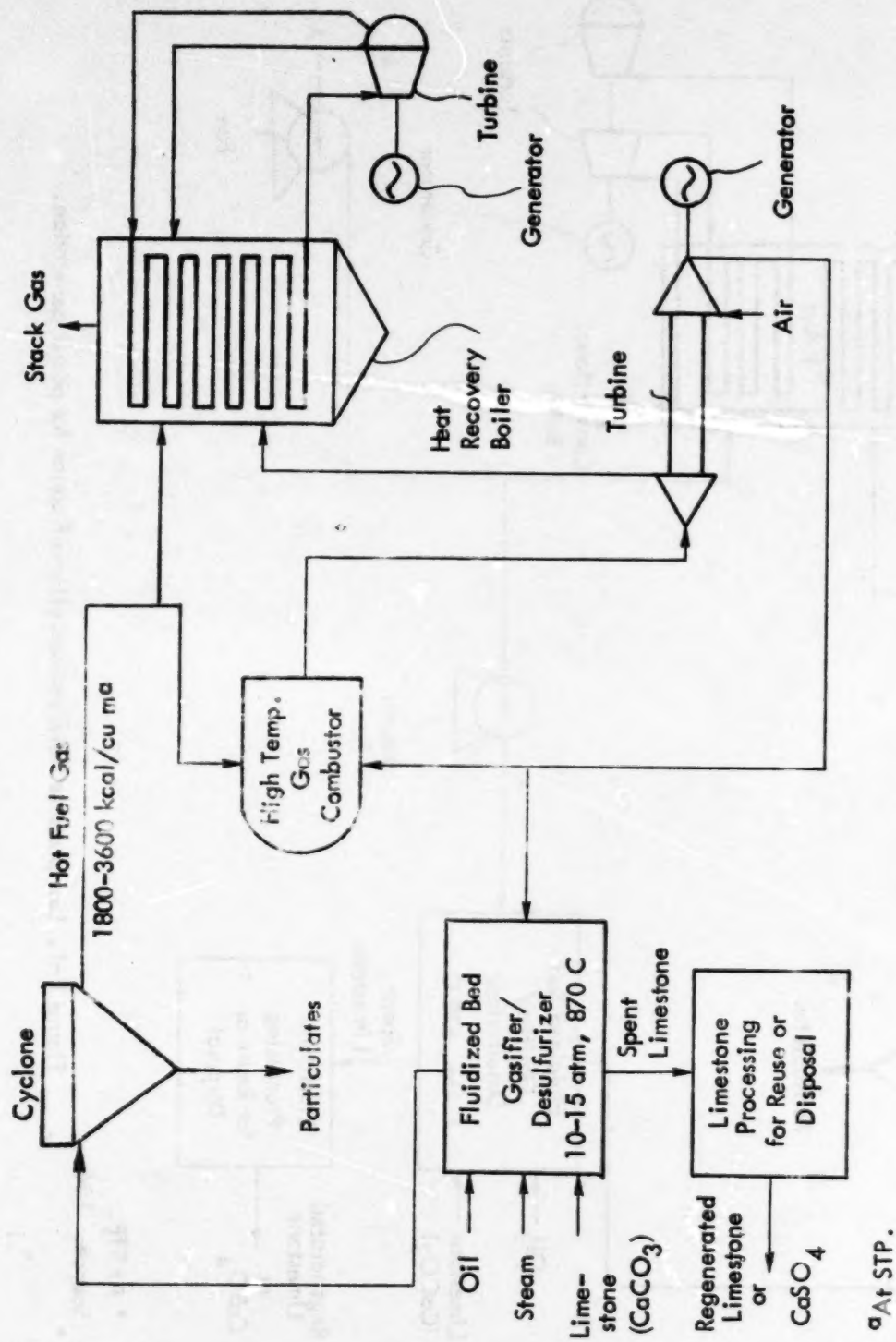
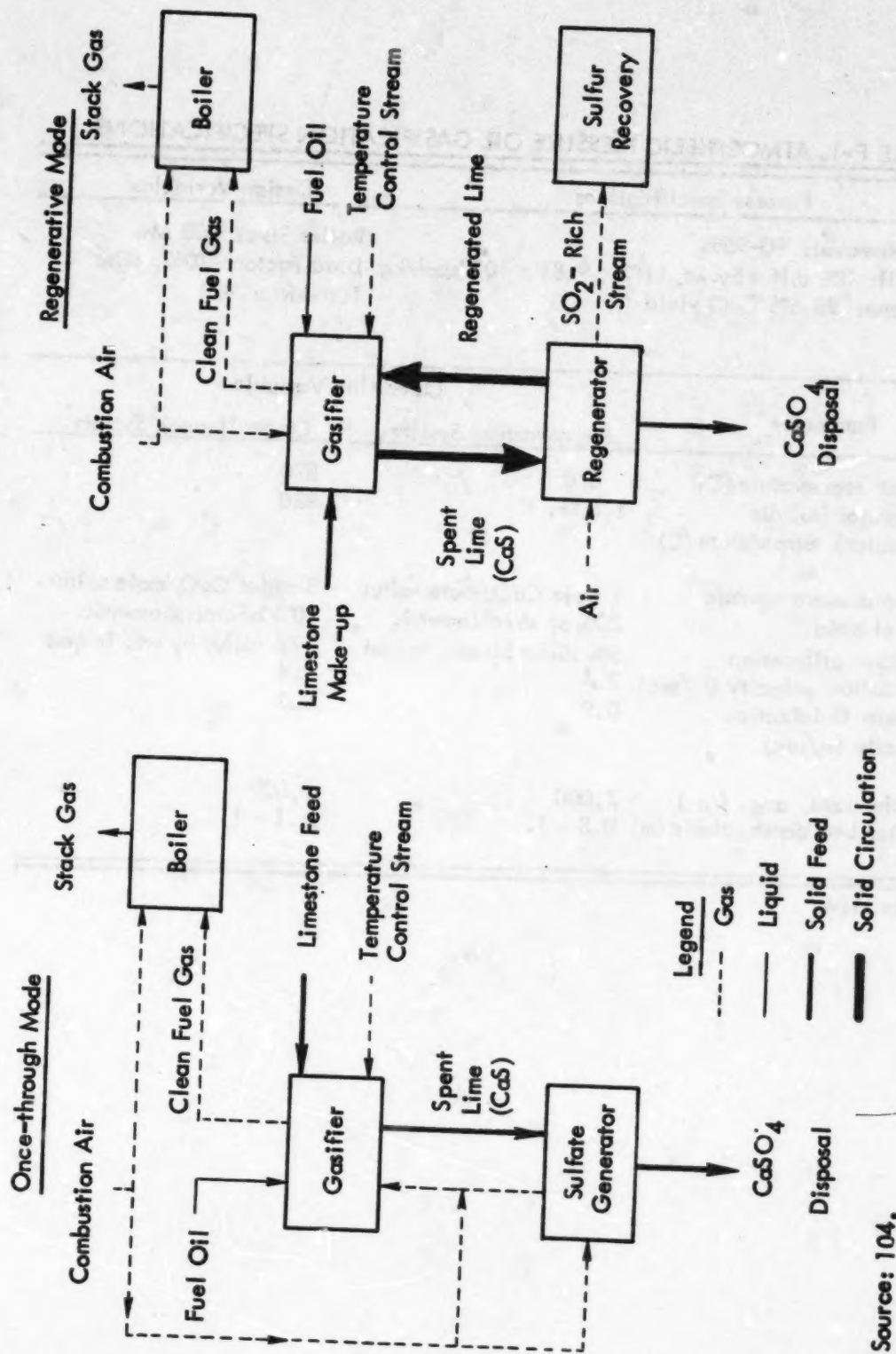


Figure F-2. High pressure fluidized bed oil gasification for power generation.

Source. 104.



Source: 104.

Figure F-3. Modes of operation, fluidized bed oil gasification plant.

TABLE F-1. ATMOSPHERIC PRESSURE OIL GASIFICATION SPECIFICATIONS

Process Specifications		Design Variables
Sulfur Removal: 90-95%		Boiler Size: 600 Mw
Fuel Oil: 3% sulfur by wt., LHV = 9.81×10^3 kcal/kg		Load Factor: 40%, 80%
Limestone: 98.6% CaO yield		Turndown: 4/1
Parameter	Operating Variables	
	Regenerative System	Once-Through System
Gasifier temperature (°C)	870	870
Regenerator (sulfate generator) temperature (°C)	1,000	820
Limestone make-up rate	1 mole CaO/mole sulfur	3 moles CaO/mole sulfur
Air/fuel ratio	20% of stoichiometric	20% of stoichiometric
Limestone utilization	5% sulfur by wt. in bed	19% sulfur by wt. in bed
Fluidization velocity (m/sec)	2.4	2.4
Minimum fluidization velocity (m/sec)	0.9	0.3
Particle sizes, avg. (μ)	2,000	1,000
Gasifier bed depth, static (m)	0.8 - 1.1	1.1 - 1.2

Source: 104.

The SO_2 stream is transported to a sulfur recovery system, and the regenerated lime is returned to the gasifier along with an approximately stoichiometric amount of fresh make-up limestone.

Once-Through Operation. The elements of the once-through operation are a gasifier vessel and a sulfate generator, or a predisposal vessel. The operation of the gasifier is the same as for the regenerative operation. The sulfate generator operates similarly to the regenerator but at a lower temperature ($\sim 800^\circ\text{C}$), so that the calcium sulfide from the gasifier is converted to calcium sulfate rather than calcium oxide. The dry calcium sulfate may be disposed of, and the gas stream from the sulfate generator is sent to the gasifier. A limestone addition rate of up to three times that used in the regenerative operation may be necessary to achieve sulfur removal of 90 to 95 percent.

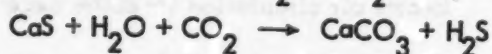
High-Pressure Combined-Cycle Gasification

The high pressure combined-cycle gasification process can be accomplished by either once-through or regenerative operation. Table F-2 lists the factors specified for the conceptual design of the high pressure fluid-bed oil gasification process. Figure F-4 shows a flow diagram of the energy balances for the high pressure fluid-bed oil gasification process.

Regenerative Operation. The high pressure regenerative process shown in Figure F-5 consists of a fluidized-bed gasifier/desulfurizer vessel, a limestone/dolomite regenerator, and a sulfur recovery section. Residual oil is injected into the gasifier vessel and fluidized-bed of lime operated at 870°C with substoichiometric air (14 to 25 percent of stoichiometric). This yields (by cracking, partial combustion, and H_2S absorption by the limestone or dolomite) a hot fuel gas of low energy value and sulfided lime or dolomite. The gas is transported to the combined-cycle plant where combustion is completed, and the sulfided lime or dolomite is sent to the regenerator. The regenerator may be designed to produce gas rich in H_2S or SO_2 and regenerated sorbent with a decreased activity. The SO_2 or H_2S stream is transported to a sulfur recovery system, and the regenerated sorbent is returned to the gasifier along with a nearly stoichiometric amount of fresh make-up sorbent.

The regeneration of calcium sulfide and the production of a high-sulfur gas for recovery can be achieved by either of two processes, as follows:

- 1) Regeneration with CO_2 and H_2O to produce H_2S :



- 2) Regeneration with air to produce SO_2 :



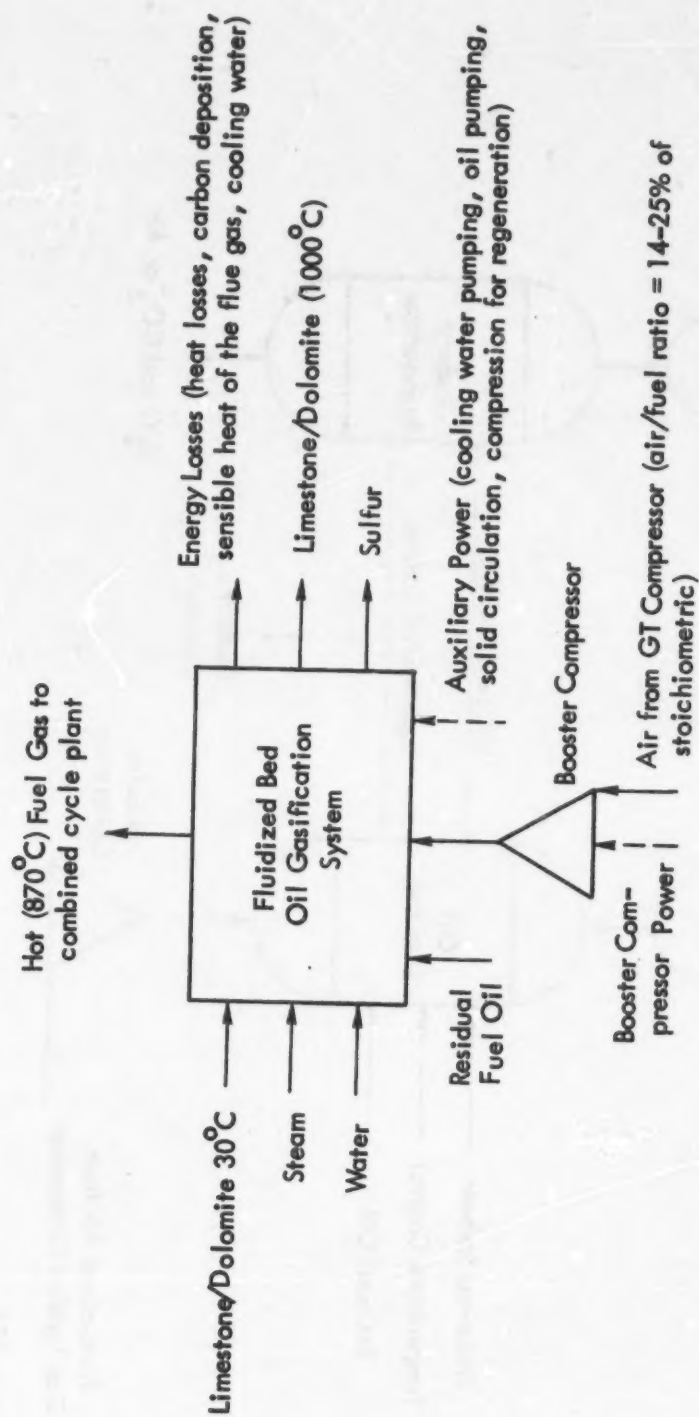
Table F-3 lists the gasification product compositions and fuel heat values for a high-pressure fluidized-bed gasification system with limestone regeneration.

TABLE F-2. SPECIFICATIONS FOR HIGH PRESSURE
FLUIDIZED BED OPERATION

Item	Specification
Plant electrical capacity	250 Mw (PACE Plant)
Capacity factor	70%
Turndown ratio	4/1
Number of gasifier modules	2
Modes of operation	Regenerative or once-through
Gasifier pressure	~ 15 atm
Pressure of gas turbine	11 atm (11.6 kgf/sq cm to turbine)
Sulfur removal	90-95%
Residual oil	3 wt % sulfur
Gasifier temperature	870 C
Regenerator temperature	600 C ^a
Sulfate generator temperature	930 C with once-through option
Air/fuel ratios	14 (minimum) & 25% stoichiometric
Lime particle diameters	500-2000 μ average diameter
Regenerative lime utilization	10%
Once-through lime utilization	35%
Limestone make-up rate	1 mole CaO/mole sulfur fed
Gasifier temperature control	Stack gas recycle, steam or water injection
Regenerator temperature control	Lime circulation rate; water injection
Sulfate generator temperature control	Excess air circulation (~ 200% excess)
Plant heat rate	2300 kcal/kwh (assumed for purposes of material balances)

^a With CO₂/H₂O regeneration; 1150 C with air regeneration.

Source: 104.



Source: 104.

Figure F-4 • Energy balances flow diagram.

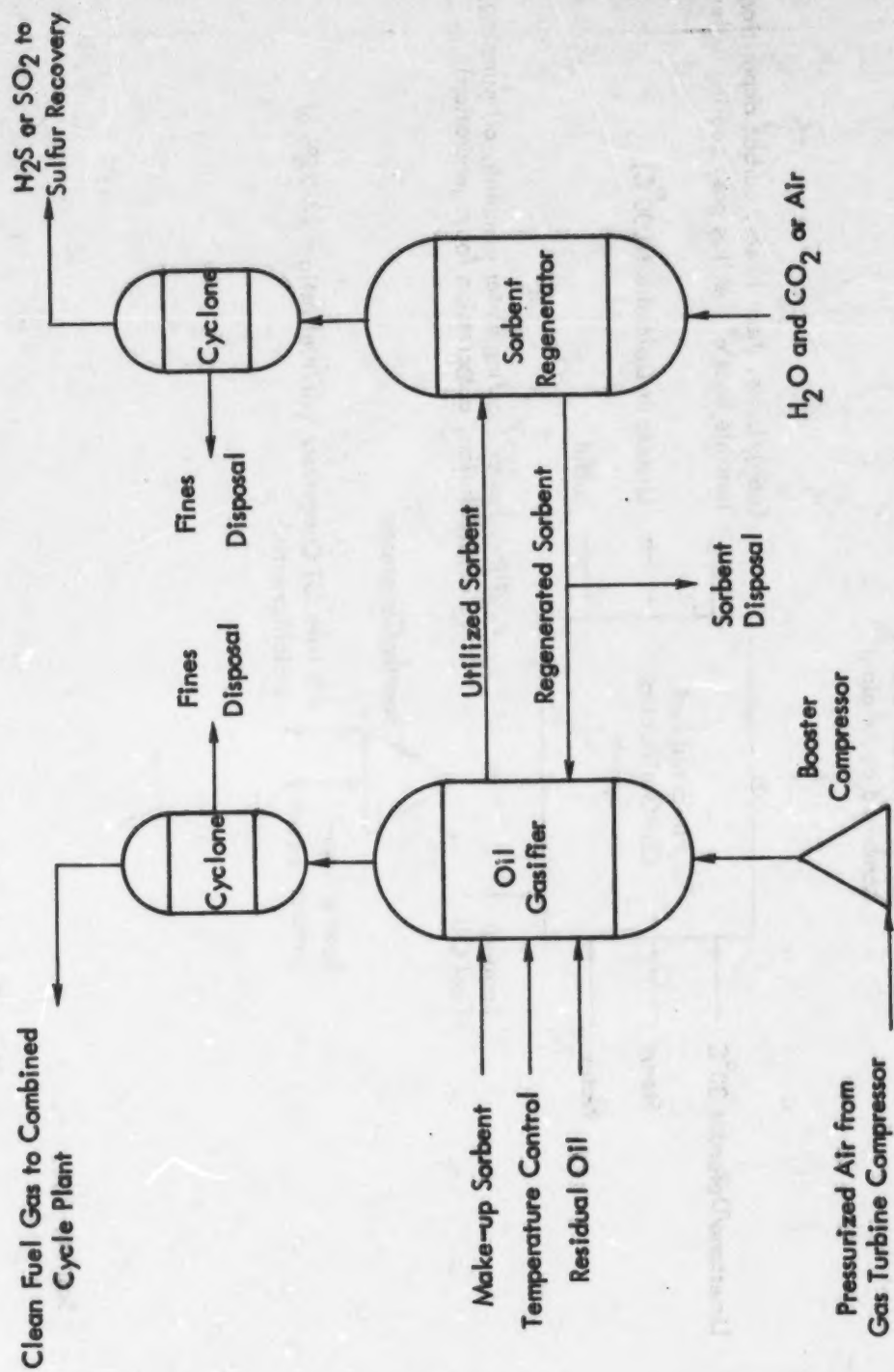


Figure F-5 . Regenerative high-pressure oil gasification process.

Source: 104.

TABLE F-3. GASIFICATION PRODUCT COMPOSITIONS

Gas	Composition (% by volume)	
	14% A/F ^a	25% A/F
N ₂	50.74	47.74
H ₂	0.82	2.64
CO	13.40	7.97
CO ₂	6.70	7.97
H ₂ O	0.00	20.56
CH ₄	9.43	6.55
C ₂ H ₄	18.86	6.55
H ₂ S	0.05	0.02
Low heating value (hot) (10 ³ kcal/cu m)	~ 70	~ 40

^a Air/fuel ratio.

Source: 104.

Once-Through Operation. If a high sorbent make-up rate is required for the regenerative processes and if high sorbent utilization can be achieved in the gasifier, a once-through system may be attractive. A flow diagram of the once-through system was presented in Figure E-4. Once-through operation would require conversion of calcium sulfide to calcium sulfate before disposal of the sorbent. The reaction is:



Process Environmental Comparison

Table F-4 compares environmental factors for power generation by oil gasification (with a conventional plant or with a combined-cycle steam and gas turbine plant) with the environmental effects of a conventional oil-fired power plant using limestone scrubbing.

The spent sorbent from the fluidized bed oil gasification/desulfurization process is dry and granular (~ 6 mm). The composition is primarily calcium oxide and calcium sulfide with small amounts of calcium sulfate—the spent stone from regenerative operation containing approximately 1 to 2 percent CaS and, from once-through operation, a projection of 30 to 80 percent CaS. Table F-5 lists some advantages of low-pressure oil gasification over stack gas wet scrubbers.

Preliminary indications suggest that the once-through operation may be somewhat more attractive to a utility than the regenerative operation.

Esso Research Center's Process (Abingdon, England)

CAFB Pilot Plant

The Chemically Active Fluid-Bed (CAFB) developed by Esso reduces sulfur oxide pollution while using high sulfur oil to produce power. The process uses a fluidized-bed of lime particles to convert the oil into a hot, low sulfur gas ready for combustion in an adjacent boiler. The process has the additional benefit of removing vanadium before the final combustion states and thus eliminating a source of internal boiler corrosion.

When oil is combusted under sub-stoichiometric conditions, the sulfur is trapped by lime as calcium sulfide:



CaS formed by the reaction of H_2S and CaO in the gasifier fluid-bed is converted back to CaO in a fluid-bed regenerator by contact with air:



The amount of regenerated lime removed is made up by the addition of fresh limestone to the combustor; sulfur is recovered during the regeneration process in several ways, such as conversion to H_2SO_4 or elemental sulfur.

TABLE F-4. ENVIRONMENTAL IMPACT COMPARISON

Environmental Factors	Conventional Oil-Fired Power Plant with Limestone Wet Scrubbing	Conventional Oil-Fired Plant with Atm-Pressure Oil Gasification	Combined Cycle Power Plant with Pressurized Oil Gasification	
	Regenerative	Once-through	Regenerative	Once-through
Plant capital investment (\$/kw)	310	300	180	160
Plant energy cost (mills/kwhr)	12.7	12.5	9.7	9.2
Limestone waste (kkg/day)	80-160	450-730	80-160	450-700
Water usage (kkg/day)	-	-	-	-
SO ₂ emission (kg/10 ⁶ kcal)	0.63	0.63	0.63	0.63
NO _x emission (kg/10 ⁶ kcal)	0.29	0.29	0.29	0.29
Particulate emission (kg/10 ⁶ kcal)	0.04	0.04	0.04	0.04
Thermal emission (% of conventional plant)	~ 100	~ 100	~ 50	~ 50
Auxiliary power & fuel (% of plant input)	2.5	2.5	7.5	5.0
Plant heat rate (kcal/kwhr)	2,400	2,400	2,400	2,300
Land requirement	large area for disposal pond	large area	more compact power plant	

Basis: 635 Mw power plant @ 1973 costs; capitalization at 15%; residual oil at \$1.79/106 kcal; gasification at air/fuel ratio of 20% of stoichiometric; limestone make-up rate of 0.5 to 1.0 times stoichiometric for regeneration and 1.5 to 3.0 times stoichiometric for once-through; for wet scrubbing a make-up rate of 1.2 times stoichiometric; NO_x emission for gasifier based on pilot plant measurements; combined cycle plant based on conventional gas-turbine technology, advanced gas turbine conditions can reduce plant costs and total emissions; gasification process consists of two independent gasifier modules.

Source: 104.

**TABLE F-5. ADVANTAGES OF ATMOSPHERIC PRESSURE OIL GASIFICATION
OVER STACK GAS WET SCRUBBERS**

1. Corrosion and fouling problems minimized in SO_2 removal process and in boiler (minimum SO_x and V)
2. No flue gas reheat required.
3. Uses crushed limestone - no limestone pulverizing system needed.
4. Simplified disposal - dry solids and no disposal pond.
5. More compact system.
6. Reduced structural costs.
7. Lower auxiliary power requirement.
8. Reduced energy cost.
9. Improved NO_x control.
10. Potential market for spent CaO

Source: 104.

The main unit of the CAFB process is the combustor and regenerator system, which is made of an insulated steel shell contained in a refractory concrete cast. The gasifier and regenerator are cavities in a single refractory concrete block. The block contains other cavities which make up the gasifier outlet cyclones, the gas transfer ducts, and transfer lines through which solids circulate. The gasifier product gas fires a 2,930 kw pressurized water boiler. The hot water is heat-exchanged through a forced convection cooling tower. The rest of the system consists of the necessary blowers, pumps, and instruments to operate the gasifier, regenerator, burner, and solid circulation system.

Batch Reactor and CAFB Experiments

Under contract to EPA's Office of Research and Development, Esso (England) investigated sulfur absorption and lime regeneration operating variables. The experimental equipment used in the study consisted of two batch reactor units and the continuous CAFB pilot plant. Changes were made to various sections between test runs as a result of experience, and to achieve specific objectives. The oils used were heavy fuel oils from Venezuela crudes obtained from the Amuary Refinery of the Crude Petroleum Co. Pilot plant runs had employed U.S. Stone BCR 1691 and a U.K. limestone from Denbighshire. Batch units had employed the latter two stones, as well as U.S. Stone BCR 1359. A summary of the experimental results appears in Table F-6.

Each batch unit contained a reactor, air and fuel systems, a flare for product gas disposal, and a gas sampling and analysis system, as shown in Figure F-6. The reactors were made of stainless steel with a refractory lining. The lower section, which contained the fluid bed, was 17.8 cm (ID) by 84 cm high. The reactors used in the original tests were not fitted with cyclones and, therefore, were used only in low gas velocity experiments. The unit has no provision for temperature control other than by adjusting the quantity of insulation around the reactor. The insulation was arranged to permit the unit to operate in the range of 800 to 900° C with air velocity of 1.2 m/sec and an excess air of over 30 percent to that required for combustion.

When operating under combustion conditions and also during regeneration of bed material, the gas from the bed was monitored directly for CO_2 , CO , O_2 and for appropriate information on combustion efficiency, sulfur removal efficiency, or sulfur release deduced. During gasification, a portion of the product gas was burned in a sample flame located just above the reactor, and the combustion products were analyzed for SO_2 , O_2 , CO , and CO_2 . The desulfurizing efficiency of the gasifier was calculated from the analysis of the fully combusted gas. The first reactors were used in the initial fuel oil screening work; the two later batch reactors were designed and constructed for studies of various operating modes.

The upper section of the reactor was redesigned to permit installation of two internal cyclones and to allow drainage of the cyclone for external sample collection. Internal cooling coils contained in the reactor allowed the temperature to be controlled independently of fuel and air rates. The type of reactor used for these studies is shown in Figure F-7.

TABLE F-6. SUMMARY OF EXPERIMENTAL RESULTS

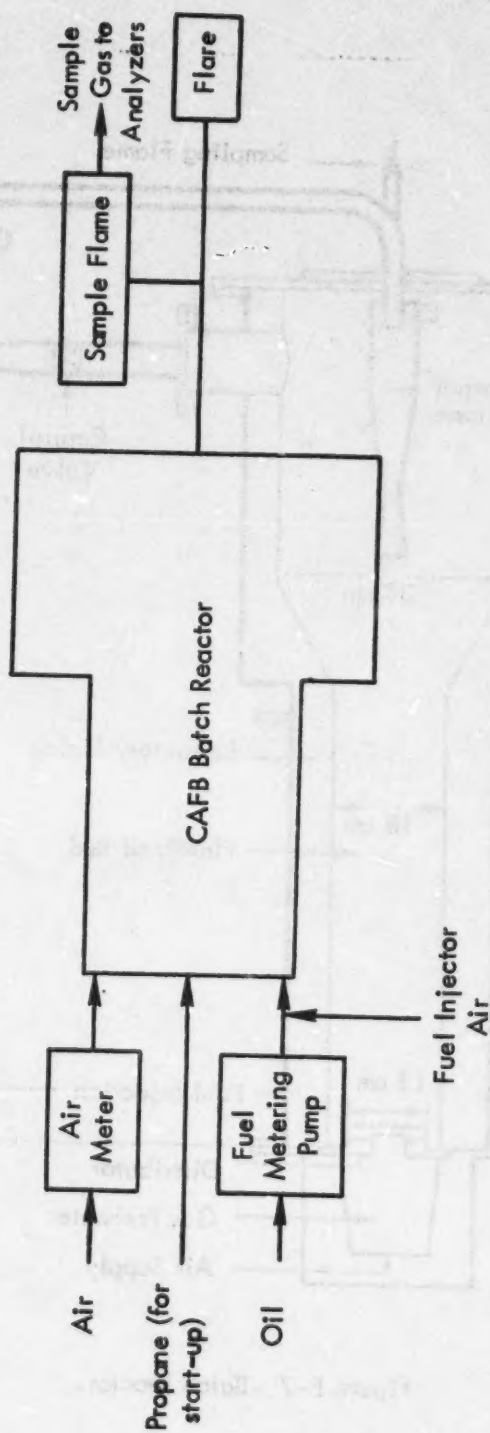
Batch Tests

1. Nearly 100% sulfur removal at 870 C, 20% air/fuel ratio, with limestone make-up rate of 1 mole CaO/mole of sulfur bed.
2. Nearly 100% of fuel vanadium removed.
3. About 20% of fuel sodium removed.
4. Clean product fuel is easily combustible with a luminous smoke-free flame.
5. Regeneration at 1000 C gives a 10% SO₂-gas product and a regenerated lime having reduced activity.

Continuous Unit

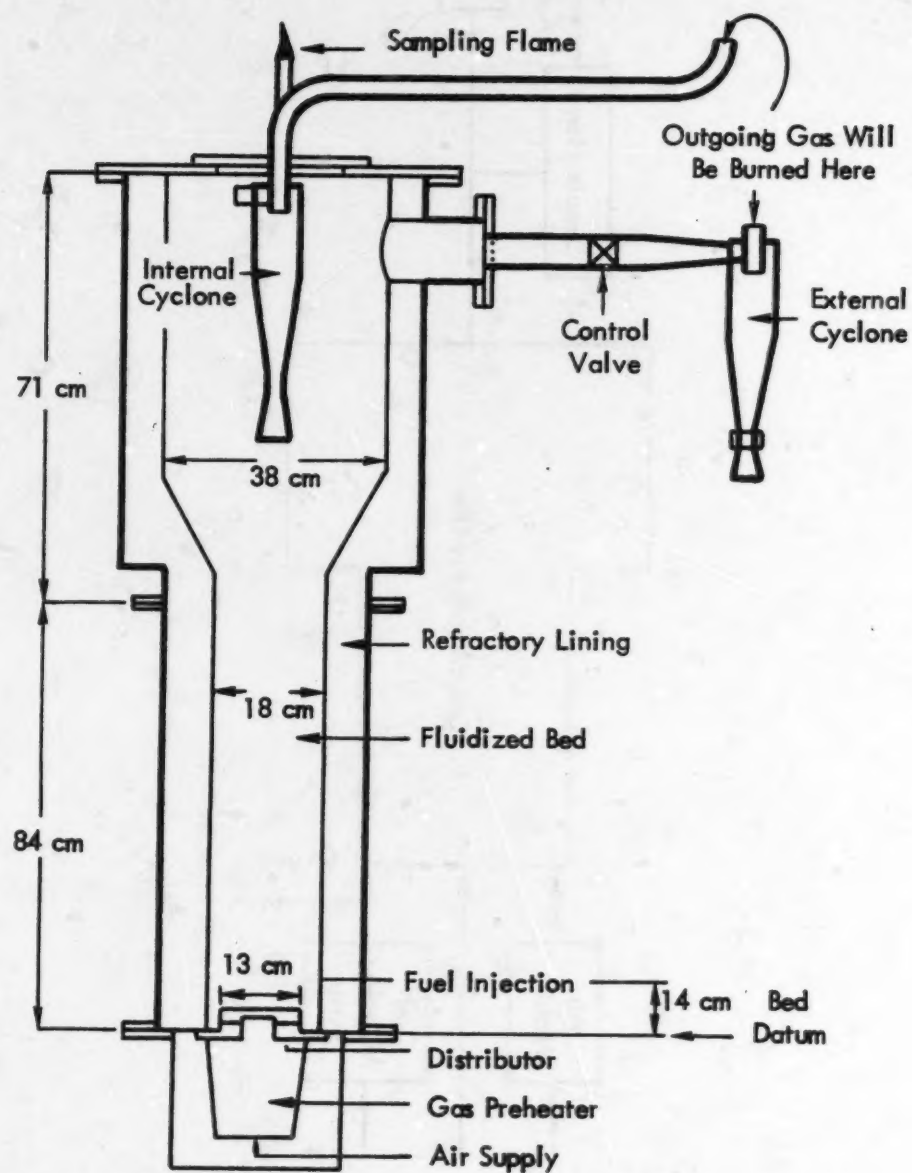
1. Results indicate superior behavior during continuous operation due to the improved temperature control.
 - Lower air/fuel ratios, down to 17% of stoichiometric, have been demonstrated.
 - 90% sulfur removal has been demonstrated.

Source: 104.



Source: 53.

Figure F-6. Esso, England batch reactor oil gasification system.



Source: 53.

Figure F-7 • Batch reactor.